Affordable Filtration Technology of Safe Drinking Water for Rural Newfoundland and Labrador

by

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Abstract

The main objective of this study is to design a cost-effective filtration system to reduce natural organic matter (NOM) in the intake water source and also to remove trihalomethanes (THMs) and haloacetic acids (HAAs) in the drinking water systems of Torbay and Pouch Cove communities near St. John's. To reduce the concentration of THMs and HAAs, a series of experiments were conducted on tap water using an inexpensive adsorbent. The results showed more than 95% removal of THMs and 35% of HAAs in the Pouch Cove drinking water using activated carbon. Another test was conducted with clean carbon without activation which shows significant removal of chloroform, bromodichloromethane, and bromoform in the THMs group and a high percentage removal of bromchloroacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid in the HAA group. Clean carbon was also used to remove total organic carbon (TOC) in the intake water source before chlorination. The results showed more than 92% removal of TOC from Pouch Cove and 65% removal from the Torbay intake water. The results showed that the formation potential of THMs and HAAs are significantly reduced due to low TOC values in the filtered water and low-cost adsorbent can be used as an effective adsorbent to supply safe drinking water to rural communities.

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List of Abbreviations

Activated Carbon	AC
Bromochloroacetic acid	BCAA
Bromodichloroacetic acid	BDCAA
Bromodichloromethane	BDCM
Bromoform	CHBr3
Canadian Council of Ministers of Environment	CCME
Chloroform	CHCl3
Dibromoacetic acid	DBAA
Dibromochloroacetic acid	DBCAA
Dibromochloromethane	DBCM
Dichloroacetic acid	DCAA
Disinfection by-products	DBPs
Filtered raw water total HAAs	FRTHAAs
Filtered raw water total THMs	FRTTHMs
Filtered tap water total THMs	FWTTHMs
Haloacetic acids	HAAs
Heavy oil fly ash	HOFA
Inductively Coupled Plasma – Mass Spectrometer	ICP-MS
Inorganic carbon	IC
Micro electron capture detector	μ-ECD

Monobromoacetic acid	MBAA
Monochloroacetic acid	MCAA
Natural organic matter	NOM
Raw water total HAAs	RTHAAs
Raw water total THMs	RTTHMs
Specific Ultraviolet Absorbance	SUVA
Tap Water Total THMs	TWTTHMs
Total carbon	TC
Total organic carbon	TOC
Tribromoacetic acid	TBAA
Trichloroacetic acid	TCAA
Trihalomethanes	THMs
Ultraviolet	UV
Volatile organic compounds	VOCs
X-ray Diffraction	XRD

Chapter 1 Background

1.1 Introduction

Water utility managers are facing numerous obstacles to protect drinking water supplies from water-borne diseases. To supply safe water, chlorine is the most common oxidant and disinfectant used to eradicate and inactivate pathogens causing such diseases. Chlorine can oxidize iron and manganese. It also removes taste and color and prevents biological re-growth in the water distribution systems. Due to its relative effectiveness as a low-cost disinfectant, more than 90% of the world water supply systems use chlorine. This disinfectant in residual form, however, reacts with the natural organic matter (NOM) present in the water, forming disinfection by products (DBPs) in the water supply system.

NOM consists of numerous organic materials such as proteins, humic substances, hydrophilic acid, lipids, carbonates and bi-carbonates. Reaction between the NOM and the residual chlorine causes the formation of more than 600 DBPs in the water supply system, among them, Trihalomethanes (THMs) and Haloacetic acids (HAAs) are the most common groups.

To protect public from exposure to these DBPs, regulatory agencies have placed limitations on their levels in the drinking water with the aim to minimize their adverse effects on human health without any microbiological water quality changes. These effects are based on the levels of DBPs and residual chlorine levels at different stages in the drinking water supply system. To improve the quality of water from conventional water

supply systems we need to introduce new technology to enhance water quality and reduce the DBPs. Activated carbon is one such filtration material for the reduction of THMs and HAAs.

Activated carbon has been effectively used for the removal of toxic chemicals, gases and unwanted contaminants from water sources. The adsorption ability of the activated carbon varies due to its porous structure. In previous studies, activated carbon has mostly been used for the removal of natural organic matter, total organic carbon, dissolved organic carbon, taste, odour, micro pollutant and heavy metals (Kim et al., 2009).

This study is aimed at the use of activated carbon adsorption capability from the carbon extracted from waste materials, to provide cost effective filtration media for small communities to reduce the concentration THMs and HAAs in the drinking water. The experiments have been conducted on tap water and under laboratory controlled conditions on raw water (Intake water) and the results are very encouraging.

In this study we used water from Torbay and Pouch Cove communities near St. John`s Newfoundland where elevated levels of THMs and HAAs are found. The reduction in the concentrations of HAAs and THMs were examined with flask(batch) and column tests.

1.2 Research Objective

The main objective of this study is to develop a cost effective filtration technology using extracts from heavy oil fly ash carbon waste residues to reduce the THMs and

HAAs concentrations in the drinking water sources to the acceptable levels recommended by US EPA and Health Canada. To conduct this study, two small communities (Pouch Cove and Torbay) near St. John's were selected.

1.3 Research Scope

This study focuses on the DBP formation in water supply system of the communities of Pouch Cove and Torbay. I focused on source of water and treatment facilities in small communities. The Pouch cove and Torbay communities do not have water treatment plants and just rely solely on the chlorination of intake water and pH adjustments. Both have high levels of concentration of THMs and HAAs according to the Department of Environment and Conservation in Newfoundland data. In the first phase, the removal of THMs and HAAs from tap water at these communities was studied by passing the tap water through the activated carbon. While in the second phase, a study was conducted on the removal of precursors causing formation of DBPs in the drinking water once the raw water is chlorinated. The removal of DBP precursors, measured as TOC was studied and a comparative evaluation was made on THM and HAA formation potential in the raw and filtered water.

1.4 Organization of Thesis

This thesis is divided into eight chapters. First chapter introduces research outline and the objective of the study. Chapter two covers a comprehensive literature review on the mechanism of formation of DBPs, their health impacts, control measures, and current and emerging technologies to reduce DBPs in the drinking water. This chapter also covers

the effectiveness of the filtration technology for small communities. This Chapter also covers statistical trend and range of THMs and HAAs in the drinking water supply systems in Canadian provinces. Chapter three, four and five are the core chapters of this thesis and describe the experimental setup, details on preparation of filter media, preparation of the adsorbent from the clean and activated carbon, and a brief description of the methods used to analyse water samples. Chapter six includes a detailed analysis of data on the removal of individual compounds within the THM and HAA groups. This chapter also describes a detailed analysis of the data on the reduction of THM and HAAs in the intake water supply system of each community with variation of TOC. The limitations of the study and major findings are concluded and recommendations for future work are outlined in the Conclusions (chapter seven) and Recommendations (chapter eight).

Chapter 2 Literature Review

2.1 Background

The water causing water-borne diseases such as cholera, typhoid and dysentery is a global issue and water distribution supply systems are unable to provide safe water supply to consumers unless these diseases-causing pathogens are inactivated in the system. Even countries such as USA and Canada with advanced water treatment technologies are facing problems to control the outbreaks of water-borne diseases.

Based on the World Health Organisation (WHO) statistics, approximately 3,400,000 people and young children under the age of five, die every year in Asia, Africa and Latin America due to the water-borne diseases (WHO, 2002). More than 100 people died and 400,000 were affected in 1993 in Milwaukee city of Wisconsin state in USA as a result of presence of cryptosporidium in the drinking water source (Mackenzie et al., 1994). Approximately 2,300 people suffered from E-coli contamination in drinking water in Walkerton, Ontario, Canada (MOE, 2002).

Historical data show that in the 15th century AD, Egyptians used chemical catalysts such as alum for coagulation and settling of suspended particles in the water as the conventional treatment method (MWH, 2005). In the early 1804, the first treatment plant was installed in Paisley, Scotland. After the introduction of chlorine as a chemical disinfectant, Chlorine and ozone were used in 1902 in the Middlekerke water supply system in Belgium and in 1906 in France (MWH, 2005).

In North America, chlorine was first used as a disinfectant in Chicago, Jersey City, as well as in Peterborough, Ontario in 1908 and 1916 respectively (Chlorine Chemistry Council, 2003; Peterborough Utility Commission, 1998).

Chlorine is now commonly used as the disinfectant in North American water systems (USEPA, 2006; Health Canada, 2007). Additionally, other disinfectants like chloramines, chlorine dioxide, ozone and ultraviolet (UV) radiation are also used to disinfect water before consumption (MOE, 2006; USEPA, 2006). A chlorine disinfectant dose is used at the last stage in water distribution system to inactivate all the microorganisms before the water reaches to the first consumer and prevent further re-growth in water supply systems. The effectiveness of the disinfectant is evaluated on the basis of its contact time and the residual chlorine concentration in the water supply system (MWH, 2005). To inactivate the microorganisms, disinfectants have different contact times which depend on pH and water temperature.

Table 2.1 shows comparison of three disinfectants with different parameters such as temperature, pH, chlorine dose, and contact time. This table demonstrates that the inactivation efficiency of chlorine and chlorine dioxide is much higher as compared to monochloramines. In order to increase the efficiency of monochloramines, increment of the dose is required.

The maximum efficiency of disinfectant in water depends upon the nature of the microorganism in the water, pH, temperature, and the working principles of the treatment plant (Sadiq and Rodriguez, 2004). The efficiency of chlorine is improved with higher

contact time and lower pH values, and these values also change with the type of disinfectants used for inactivation of the microorganisms.

Table 2.1 Disinfectants and inactivation efficiency of microorganisms (Sadiq and Rodriguez, 2004)

Disinfectant	Organism(Group)	Ct(mg.min/l	pH	Temp(c)	Inactivation (%)	References
Chlorine	V. cholerae	60	7.0	20	>99.99	Clark et al.(1994a,b)
	E.coli(B)	2.2	7.0	5	>99.999	Rice et al.(1999a)
	C.jejuni(B)	.1	6.0	4	>99.999	Blaser et al.(1986)
	Rota virus(V)	.13	6.0	5	~99.999	Berman Hoff(1984)
	MS2coliphage(V)	2.0	7.0	5	~99.999	Berman et al (1992)
	G.lamblia(P)	15	6-7	25	~99	Clark et al.(1989)
	E. intestinalis	16-32			~99	Rice et al.(1999c)
Mono-chloramines	C. jejuni (B)	15	8	5	>99	Blaser et al.(1986)
	Rota virus(V)	>3600	8.5	5	~99	Berman and Hoff (1984)
	MS2coliphage (V)	2.0	7.0	5	~99	Berman et al (1992)
Chlorinedi-oxide	Rota virus(V) Rota virus(V)	≤0.5 ≤0.25	6.0 10.0	5 5	>99 >99	Berman and Hoff (1984)

B: Bacteria, V: Viruses, P: Protozoa

Once disinfectants are added in the water, some by-products or DBPs are formed in the presence of natural organic matters (NOM) in the water supply system. The NOM are classified into two groups. The first group consists of non-humic substances and are combination of organic compounds such as ammonia, fat, hydrocarbons, carbohydrates, wax, resins, and low molecular acids and the second group is more complicated according to its chemical structure and heterogeneous humic solutes. The parameters such as NOM, pH, temperature of water, chlorine dose and bromine concentration have influence of increasing the DBPs in water (Zhang et al., 2008). Most common DBPs are Trihalomethanes (THMs), Haloaceticacids (HAAs), Haloacetonitriles (HANs),

Haloketones (Hks), Carboxylicacids, Aldoketoacids, Aldehydes, Oxyhalides, and Cyanogen halides (Krasner,1999). More than 600 DBPs have been found in water systems (Richardson et al., 2007).

Drinking water is supplied to consumers through the distribution systems and most of these systems have DBPs. The Canadian regulatory agencies have developed guidelines for THMs as 100µg/L and for HAAs as 80 µg/L and other countries follow their own guidelines for drinking water (Health Canada,2007; USEPA,2006; WHO,2004).

The chlorine dose is given after screening, coagulation, flocculation, sedimentation and filtration, at the last stage of water supply system. The reaction between the NOM and disinfectant dose like chlorine is considered the main cause of DBPs in water systems and depends on contact time, pH value, seasons of the years, and water temperature. A recent study showed that higher pH value causes higher concentration of THMs and lower concentration of HAAs, and other components like chlorine dose, contact time and temperature also contribute in the formation of THMs and HAAs (Guo, 2011).

The characteristics of NOM depend upon the geographic, topographic and the catchments area of the source water used by the water distribution system (Ye et al., 2009). The concentration of NOM varies throughout the year and it is not easy to be measured directly. The NOM assessment is based on the combination of total organic matter, dissolved organic matter, ultraviolet absorbance at 254nm wave lengths and molecular weight ranges from 500 to 5500 Dalton (MWH, 2005). The microorganisms

like pathogens are inactivated by chlorination to provide safe drinking water to consumers (Panyapingyopol et al., 2005).

The characteristics of DBPs mostly depend on microbiological and geological sources of water (Kim, 2009, Ye et al., 2009). The higher and lower molecular weight of NOM consists of activated aromatic rings, phenolic hydroxyl, conjugate double bond and hydrophobic, aliphatic ketones alcohols respectively (Liang and Singer, 2003). The specific ultraviolet absorbance (SUVA) values are high in hydrophobic and low in hydrophilic compounds (Uyak and Toroz, 2007).

The individual THM compounds are Chloroform ($CHCl_3$), Bromodichloromethane ($CHCl_2Br$), Dibromochloromethane ($CHClBr_2$) and Bromoform ($CHBr_3$). THMs are considered based on their composition (IRIS, 2006).

The mechanism of formation of DBPs in the water depends on the NOM and their concentration in water before adding disinfectant as well as the retention time in the water supply system before it reaches to the first consumer.

There are several studies concerning the formation of DBPs and their adverse health impact but there has not yet been much attempt to reduce impact on human health (Hoffman et al., 2008). Smith and El-Deen (2009) conducted a 15-month pilot program covering all seasons and found that total THMs were at maximum throughout the year except in the winter seasons while HAAs were high in spring and fall and low in summer and winter.

To improve the risk assessment of DBPs, it is very important to monitor key parameters such as contact time in the plant, UV absorbance and residual chlorine in the system (Mouly et al., 2010). The reduction of THMs and HAAs and their interactions in water distribution system need to be considered further (Francis et al., 2010).

Legay and Rodriguez (2011) developed a model to evaluate the amount of THMs and HAAs in the distribution system and its effects on human health. These studies demonstrate that there is a high correlation of DBPs with premature child birth, birth defects and fetal loss (Bove et al., 1995; Hinckley et al ., 2005a; Lewis et al ., 2006; Hoffman et al., 2008;Grellier et al., 2010). In epidemiological studies, it is very important to accurately assess the exposure and measure the value of THMs and HAAs otherwise there is potential for errors in the risk assessment modelling (King et al., 2004; Hinckley et al., 2005b; Chang et al., 2010; Wei et al., 2010). Colon, bladder and rectum cancer are also linked with the exposure of DBPs due to chlorine in the system (Mills et al., 1998).

A recent study on 13 cities in China found the concentration of THMs and HAAs in most water distribution systems range from 20 to 448 and 29 to 259 μg/ L respectively (Zhang et al., 2011). In Taiwan, Chang (2010) conducted study on 86 water distribution systems and main water sources and found high concentration in winter and summer for HAAs and high level of THMs during the summer. The THMs concentration increased with increase in the chlorine dose, retention time and temperature. (Lu et al. 2009 a, b; and Tokmak et al., 2004). In another study, detailed experiments on THMs and HAAs in 41 water distribution systems in 6 cities of China showed significantly high concentrations in the summer as opposed to winter seasons (Ye et al., 2011).

Mostly water reaches the supply system through pipes, stored in the water supply tanks and then distributed to the household units. It is important to estimate the duration for which water stays in the distribution pipes before it reaches to the consumers (Baribeau et al., 2004, Dion-fortier et al., 2009). The research showed an increase in THM concentration with time in storage tanks and the pipe systems (Dion -Fortier, 2009; Weinberg et al., 2006). As the water stays in the pipelines in off hours i.e., midnight to the morning, it allows extra reaction time between the free NOM and free residual chlorine, causing increased concentration of DBPs in the water supply system (Sadiq and Rodriguez, 2004)

Boiling water has significant effects on the reduction of THMs and HAAs. As boiling time increases, THMs concentration reduces by almost 90% but boiling does not has a significant effect on the removal of HAAs (Kranser et al., 2005). After boiling water for 1, 2, and 5 minutes, the total THMs were reduced by 75%, 84%, and 97% respectively, compared to the total HAAs which have reduction of only17%, 22%, and 23% respectively (Kranser et al., 2005).

The goal of this study is to develop an inexpensive and effective filtration technology to reduce concentration of THMs and HAAs in the drinking water in the small communities of St. john`s Newfoundland with the help of activated carbon or clean carbon as filtration media. In 1550 B.C. wood char was used as carbon for the medical purposes as an absorbent. In 1785 carbon was used to accumulate the unwanted contaminants from the water and in late 1800s activated carbon was first time used as filtration media. First GAC filtration was installed in Europe in 1929 and in USA in 1930.

In 1970 GAC was very effective for removal of wide spectrum of harmful chemicals and gases from the water sources.

Activated carbon has porous structure surrounded by carbon atoms and therefore is a material with adsorbent capability. The most important consideration to investigate its chemical characterization is its porosity, how adsorption takes place in pore size (March& Reinoso, 2006). Raw materials can be manufactured from carbonaceous materials like coal, peats, wood, coconuts, vegetables, animals and minerals origin based on its chemical and physical characteristics. The activated carbon is produced on the basis of carbon amount, mineral matter and sulphur content, availability, cost, and shelf life (Kroschwitz et al., 1992).The physical methods generally involve carbonization and activation stages (Singh et al ., 2008).The organic removal in GAC can be influenced by media size of GAC, uniformation coefficients(UC), EBCT, and pH(Graece et al., 1987).

Chemical activation (potassium hydroxides, phosphoric acid, zinc chloride) are effective at decomposing the structure of the raw material and forming micro pores (Marsh & Reinoso, 2006).To manufacture the activated carbon from the raw material, both chemical and physical techniques can be used. GAC filters are commonly used during drinking water treatment for the removal of the unwanted dissolved organic carbons, micro pollutants, halogenated hydrocarbons, taste and odour compounds by adsorption (Velten et al., 2007). In the previous studies mostly GAC was used for the removal of natural organic matter (NOM) and precursors of disinfection by products. Adsorption by activated carbon is one of the best treatment methods for the removal of NOM from the water (Faust,S.D., 1999). The effectiveness of activated carbon

adsorption depends upon the particles size, surface area, adsorbed concentration, pH, and redox condition or other water quality parameters (Fairly et al., 2006).

2.1.1 Chemistry of Chlorination

Chlorine is a strong oxidizer and it is used in the form of free chlorine or OCl^- and sodium hypochlorite (NaOCl). The reaction between water and chlorine forms hypochlorous acid (HOCl), hydrochloric acid (HCl), and hypochlorite ion (OCl)as shown in equation 1 and 2(Sawyer et al., 1994).

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \quad (1)$$

$$HOCl \leftrightarrow H^+ + OCl^- \quad (2)$$

The free chlorine concentration is sum of dissolved gas (Cl_2), hypochlorous acid (HOCL), and hypochlorite ion (OCl^-). Sodium hypochlorite ionizes in water to yield hypochlorite ion(equation 3).The hypochlorite is in equilibrium with hydrogen ions (H^+),

$$NaOCl \rightarrow Na^+ + OCl^- \quad (3)$$

The amount of chlorine in the water source system depends upon the halogens, organic and humic compounds in the water supply system, for reduction (Sawyer et al., 1994).

The chlorine residual is the net amount of chlorine in the water after it reacts with chemicals and kills microbes. When chlorine is added to raw water, chemicals present in the raw water begin to react with chlorine. The difference between the chlorine dosage and the chlorine residual is called chlorine demand. Chlorine existing in combined

chemical forms with ammonia or organic nitrogen compounds is referred to as combined available chlorine or combined residual chlorine. When all of ammonia has been consumed and all of the combined chlorine has been oxidized, the chlorine added become equal to the chlorine residual and this is available as free chlorine.

2.1.2 Occurrence of Disinfection By Products (DBPs)

Chlorine is the most widely used disinfectant in water treatment system. When disinfectant reacts with the NOM in the drinking water sources it leads to formation of DBPs. In disinfected drinking waters, the most common and dominant DBPs by weight are THMs and HAAs (Singer et al., 2002; William et al., 1995).There are four compounds within THMs and nine compounds within HAAs groups. These compounds are briefly discussed in the following sections.

2.1.2.1 Chloroform ($CHCl_3$)

Chloroform is clear, colourless volatile liquid with pleasant odour. It is used primarily in the manufacture of the refrigerant, chlorodifluoromethane and in the production of fluoropolymers (ATSDR, 2011). Chloroform is considered to have an average oral toxicity in rats with a dose of 0.45 to 2.0 g/kg bw (Kimura et al., 1971; Chu et al., 1980). Mice are affected by an oral dose of chloroform ranging from 36-1366 mg/kg body weight (IPCS, 1994a). Based on a dose of 30 and 60 mg/kg bw given to rats and mice, it was determined that there was no effect on the rats but the mice sustained liver damages (Keegan et al., 1998). Chloroform is categorized as a Group II probable carcinogen for human (WHO, 2000: IARC, 1991).

2.1.2.2 Bromodichloromethane (BDCM)

BDCM is water soluble, non-flammable and is used in laboratory reagents, chemical industries for manufacturing organic materials, mineral salt separations, flame retardants and fire extinguishers. The new Canadian guideline for BDCM in drinking water is 0.016mg/L (CDW, 2006).

In a study of BDCM, dose was given to the female rats and mice for 120 hours. Female rats with an average intake of 150-300 mg/kg bw/day had hepatotoxic (liver) and nephrotoxic (kidney) effects as compared to female mice who had only hepatotoxicity with 75-150 mg/kg bw/day dosage (Thornton-Manning et al., 1994).On the basis of animal experimental data, BDCM is classified as carcinogenic for humans; however no human data are available (Health Canada, 1994; NTP, 2011). BDCM causes tumour in animals at very low doses (IPCS, 2000).

2.1.2.3 Dibromochloromethane (DBCM)

DBCM is of heavy yellowish colour, used in the chemical industries in the form of aerosol propellants, refrigerants, fire extinguishing agents and pesticides. DBCM is considered carcinogenic for humans on the basis of animals experiments (NDES, 2006). DBCM guideline for water is not available (Health Canada, 2003b).

2.1.2.4 Bromoform

Bromoform is a yellowish liquid and has very limited carcinogenic effects based on animal experiment; no data however is available for humans, which is considered

group II D carcinogen for humans (IARC, 1999; Health Canada, 1994). No drinking water guidelines are available for bromoform (Health Canada, 2003b).

2.1.2.5 Monochloroacetic acid (MCAA)

MCAA is colourless with a sour odour and is available in the crystal form (Cheminfo.2003b). It is used for the preparation of glycine, phenoxyacetic acid, amphoteric surfactants, synthetic caffeine, dyes, cellulose ethers, thiglycolic acid and bacteriostats (Lewis, 2001; Koenig et al., 2002; Morris and Bost, 2002). Under controlled laboratory conditions with high concentrations, MCAA biodegrades into carbon dioxide within 10 days at 29 $^{\circ}$C (Boethling and Alexander, 1979). In a previous study, a single dose of 225/mg/kg/body weight given to hamsters identified that the liver, kidney, spleen and intestine stored maximum amount of MCAA (Saghir et al., 2003; Kaphalia et al., 1992). It was observed that urine is the only source to have minimum amount of MCAA in the body of rats based on single dose through ingestion pathways (Saghir et al., 2003; Kaphalia et al., 1992).The National Toxicology Program, conducted on 3 volunteers who consumed 300mL of .05% MCAA for a period of 2 months (2mg/kg body weight per day) showed no significant health effects (NTP, 1992). However, 50 to 500 mg/kg of body weight dose of MCAA is harmful for human beings.

2.1.2.6 Dichloroaceticacid (DCAA)

DCAA is pungent in odour and it is colourless to yellowish (Budvari et al., 1996). Recent research demonstrates that the clinical toxic genetics of DCAA is interpreted particularly in the light of it use as an investigational drug.(Stacpoole, 2011). DCAA is

used as astringent, fungicide, medical disinfectant test reagent for analytical analysis and organic materials treatment such as lactic acidosis (Koenig et al., 2002). Studies demonstrate that a single oral dose of DCAA and its distribution to young rats affects muscles (11.9%), liver (6.19%), gastrointestinal tract (3.74%), fat (3.87%), kidney (.53%) and other organs including brain, heart, bone, skin, lung and testes (9.5%). DCAA lipophilicity (non polar solvent) cannot be measured when the pH value is close to the blood pH of 7.4 (James et al.1998; Schutz et al.1999). In the study conducted by Izumi et al, (2003), the patients with genetic disorders such as hypercholesterolaemia were treated with DCAA for 120 days and it was observed that the patients developed muscle weakness and loss of reflexes in that period. Human exposure of concentrated DCAA in the work place has also been determined to cause pulmonary oedema. (Cheminfo, 2003c).

2.1.2.7 Trichloroacetic acid (TCAA)

TCAA is colourless with a pungent odour (Ashford, 1994; Budavari et al., 1996). The applications of TCAA include laboratory reagents, herbicide, soil sterilizer, organic chemicals and antiseptic (Meister, 2002). For corneal disease TCAA is used as a medication with 10-25% aqueous solution as well as for external root dentistry and skin diseases (Lewinstien and Rotstein, 1992; Koening et al., 2002).TCAA severely affects skin and causes irritations in the eye from dermal and ingestion exposure at high concentrations (Cheminfo, 2003). Decrease in the birth weight due to elevated exposure to DBP is indicated by urinary TCAA (Wen-Shan et al., 2012).

2.1.2.8 Monobromoacetic acid (MBAA)

MBAA is a colourless solid of hygroscopic crystalline shape and its applications include abscission of citrus fruits and as an organic synthetic material (Lewis.2001). In a study, the oral dose of 50 mg/kg body weight/day given to 3 male rats produced no significant changes (Jones et al., 1981). Studies on human to MBAA have not yet been conducted (IPCS, 2000).

2.1.2.9 Dibromoacetic acid (DBAA)

DBAA is available in the form of a hygroscopic crystal (U.S. EPA, 2005a). A dose of 250 mg/kg bw of DBAA given to the rats for 5 day showed no significant accumulation in testicular fat and lipophilicity (non polar solvent) is minimum when blood pH is 7.4. Plasma was also tested in female and male rats and due to high metabolism and excretion adsorption, limited effects were seen in the male rats. Plasma concentration in female rats reached maximum in half an hour and then declined in the next one and a half hours (U.S EPA, 2005a; Christian et al., 2001; Schultz et al., 1999). No research has been yet conducted on humans (IPCS, 2000).

2.2 Factors Affecting DBP Formation

The formation of THMs and HAAs varies according to the source of water. Surface water provides higher concentration of DBPs compared to the ground water. THMs are more stable than HAAs and the growth rate of HAAs is faster than the THMs (Singer et al., 2002). HAAs are neutralized as pH value increases even with very low

concentration of disinfectants in the water supply systems (Singer et al., 2005; Baribeau et al., 2006).

Formation of DBPs in the water supply system depends on pH value, contact time of residual chlorine, water temperature, NOM and residual chlorine level (Baribeau et al., 2006). To maintain safe water quality for consumers, we should have a good knowledge of the types of microorganisms in the water and their counts, sizes and materials of the pipe and storage tank, sediments in the pipe, NOM, the disinfectant dose, and treatment technology (Singer et al., 2005; Baribeau et al., 2006).

2.2.1 Reaction Time

The chemical stability of DBPs and its concentration varies in the water as the retention time increases in the water supply system. Due to biodegrading effect, long retention times, and availability of free chlorine prior to exhaustion, the concentration of HAAs and THMs increases but in some cases the HAAs values decrease to zero for long distance occupants in the water supply system but it does not have any effect on the THMs (Reckhow & Singer, 2011).The concentration of THMs and HAAs increases as the reaction time of the NOM and disinfectant increases (Xie, 2004). The level of THMs increases from the water distribution system to the first consumer but reduces towards the last consumer. This is due to longer retention time, and the concentration of HAAs is low in the beginning but very high at the end point (Rodriquez et al., 2005). Due to biodegradation of chlorine, the level of HAAs decreases in the water distribution system in the summer at extreme end of the system (Baribeau et al., 2006).

2.2.2 pH

As the pH increases in the water distribution system, THMs increase and HAAs decrease, but it is important to note that the value of pH has different effects on each compound of HAAs. For example DCAA does not change with the change in pH values compared to TCAA which reduces with the increase in pH (Reckhow & Singer, 2011). With the significant increase in pH value above 7 to 8, the THMs increase but HAAs reduce because HAAs are decomposed at high pH value compared to THMs (Reckhow & Singer, 1985; Liang & Singer et al., 2003).

2.2.3 Temperature

During warmer months of the year, the concentration of total THMs (TTHMs) and total HAAs (THAAs) is at its peak in the water distribution system (Baribeau et al., 2006). The formation of TTHMs and THAAs increases as the temperature rises. Pilot study in a controlled condition shows that the concentration of chloroform increases with the increase in the temperature, but DCAA and TCAA do not show much change with the temperature. Biodegrading effect in HAAs increases as temperature increases (Reckhow and Singer, 2011). In the summer months, the efficiency of chlorine decreases with higher temperature. As a result, the amount of the chlorine dose required also increases in the water distribution systems. The reaction rate between NOM and disinfectants is higher in summer than in the winter season.

2.2.4 Chlorine Concentration

Residual chlorine is directly proportional to DBP formation (Xie, 2004). The concentration of THMs increases as dose of disinfectants increases (Reckhow and Singer, 2011). Minor changes in disinfectant in the water distribution system do not have any major impact on the formation of DBPs in the system. A study reveals that when the residual chlorine is reduced to 0.3 mg/L in the system, the formation of DBPs is also relatively low (Reckhow & Singer, 2011). Chlorine concentration also decreases because of corrosion, biofilm and scaling in the pipelines (Rossman, 2006; Al-Jasser, 2007).

2.3 DBPs issues in Newfoundland Water Supply System

In urban areas, 75% of Canadians use drinking water supplied by a municipal water supply system (Statistics Canada, 2008). Canadians are exposed to DBPs in their life time through municipal water supply system (Health Canada, 2008).

Table-2.2 lists the means, standard deviations and concentration range of THMs and HAAs in the drinking water supply systems in Canadian provinces. As demonstrated in Table 2.2 and Figure 2.1, the highest mean THMs are found in the Manitoba as 164.9 µg/L and Nova Scotia as the second highest as 110.2µg/L while British Colombia has the lowest mean value of 38.9µg/L. In terms of mean HAAs, Nova Scotia has the highest value as 116.2µg/L, while Newfoundland has the second highest values as 107µg/L.

Table 2.2 Total THMs and THAAs in Canadian drinking water systems (values in µg/L)

Province	Period	Number of water treatment plants (WTP)	Total THMs			Total HAAs		
			Mean	Range	Std	Mean	Range	Std
Ontario(ON)	2000-04	179	40.9	.5-343	39.9	28.6	.4-244	28.9
Quebec(QC)	2002-06	622	42.5	0-565	53.3	41.2	3.9-166	36.2
Manitoba(MB)	2001-06	74	164.9	.7-640.	110.9	72.4	12-249	76.1
Saskatchewan(SK)	2002-06	204	95.3	4-445	71.8	51.8	1-238	70.8
Alberta(AB)	2000-05	449	61.5	.6-447	66.0	38.4	3-141	39
British Columbia(BC)	2001-05	13	38.4	9-116	22.7	54.4	11-117	21
Nova Scotia (NS)	1999-04	24	110.2	2-640	84.9	116.2	8-602	119
Newfoundland and Labrador(NL)	2001-07	467	77.3	0-470	79.5	107.8	0-507.5	103
New Brunswick(NB)	1993	4	62.1	4.1-146	45	85.7	10-398	96.1
Prince Edwards Island(PEI)	2003-06	-	3.5	1.4-5.9	.96	N/A	N/A	N/A

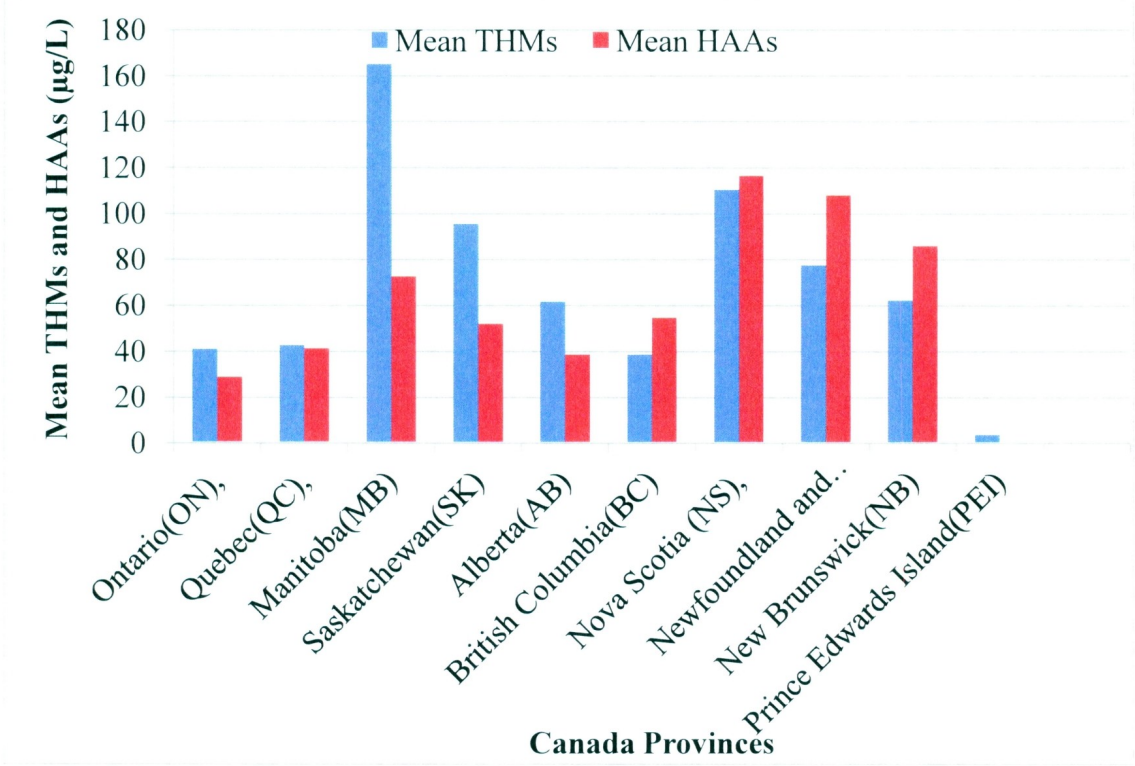

Figure 2-1 THMs and HAAs in different provinces in Canada

The Department of Environment and Conservation in Newfoundland regularly monitors THMs and HAAs in the water supply systems (MOENL, 2011) in the province. The results are plotted in Figure 2.2 and Figure 2.3. As demonstrated in these Figures, THMs and HAAs in various communities in the province are higher than the Health Canada guidelines of 100µg/L for THMs and 80µg/L for HAAs; the THMs level in few communities even exceeds 400µg/L. More than one third communities in the province have higher HAAs level than Health Canada guidelines, and 27 communities have even higher than 300 µg/L HAAs in the water supply systems.

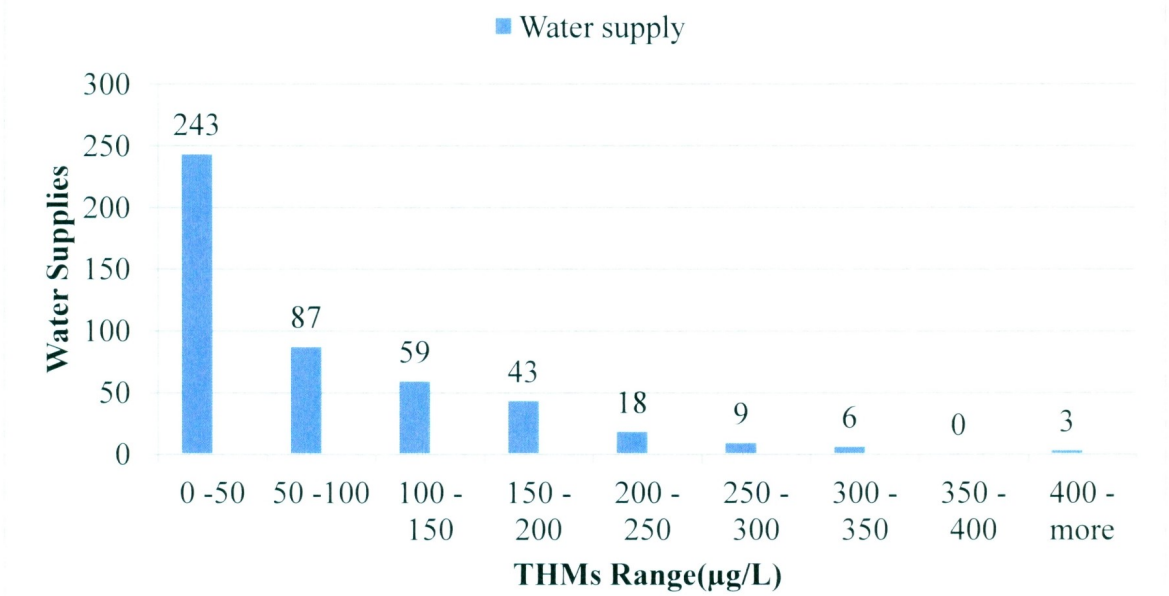

Figure 2-2 Distribution of THMs in Newfoundland & Labrador Communities (MOENL,2011)

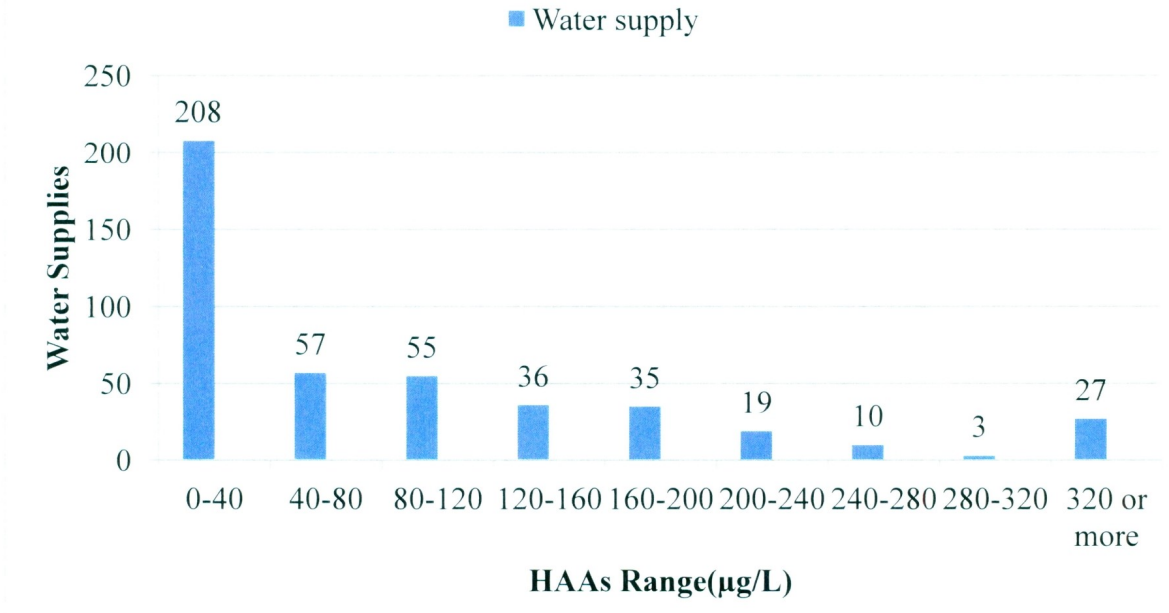

Figure 2-3 Distribution of HAAs in Newfoundland & Labrador Communities (MOENL, 2011)

Chapter 3 Water Sample Collection and characterization

St John's is the capital city of Newfoundland and Labrador with a population of approximately 125,000. The province has a number of smaller communities. This research focuses on two small communities, i.e., Torbay and Pouch Cove, close to the capital city; these communities have high concentration of THMs and HAAs in the drinking water.

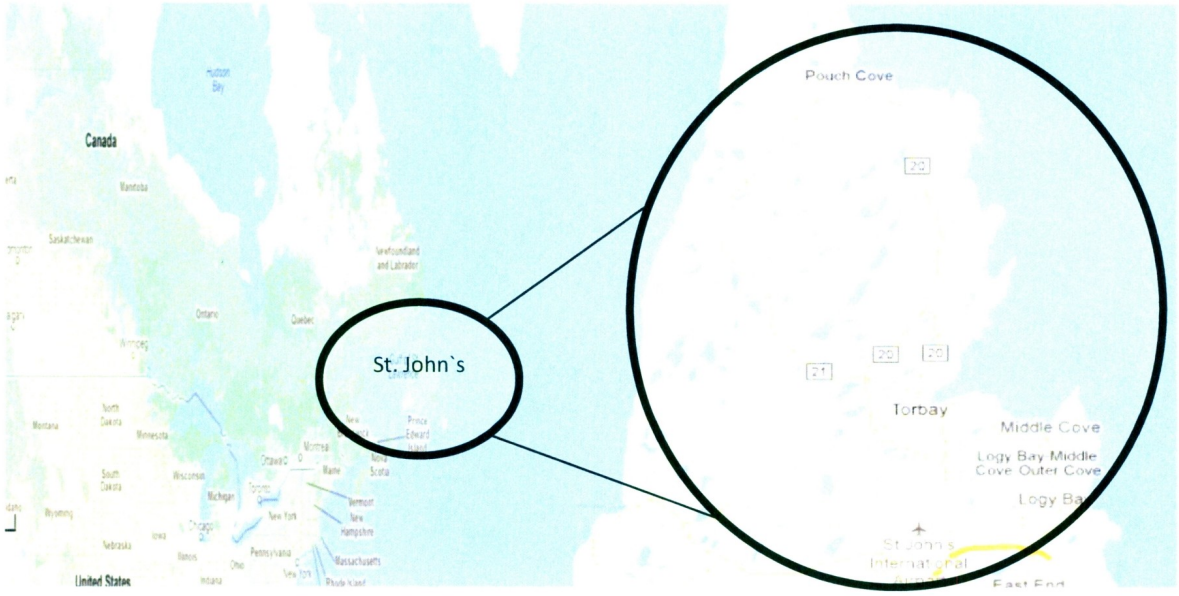

Figure 3-1 Location map of St. John's Newfoundland

The Community of Torbay is located 15 km north of St. John's. According to the 2011 census, the total population of Torbay is 7,397 which have considerably increased since 2006, when the population was recorded as 6,281. The community is served by a small water supply system. The main source of raw water in the community is from North

Pond, as shown in Figure 3.2. The raw water from the pond is chlorinated with a gas hypo booster system, and the lime is used to control the pH values between 6.5 and 8.5 as per Canadian guidelines.

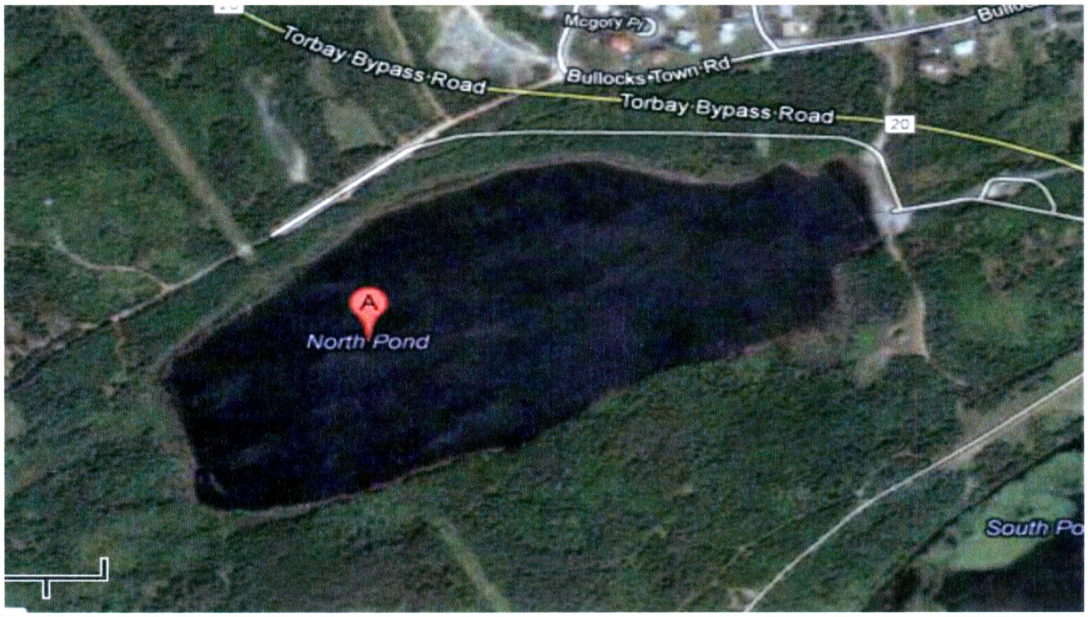

Figure 3-2 North pond inTorbay Community where sample was collected

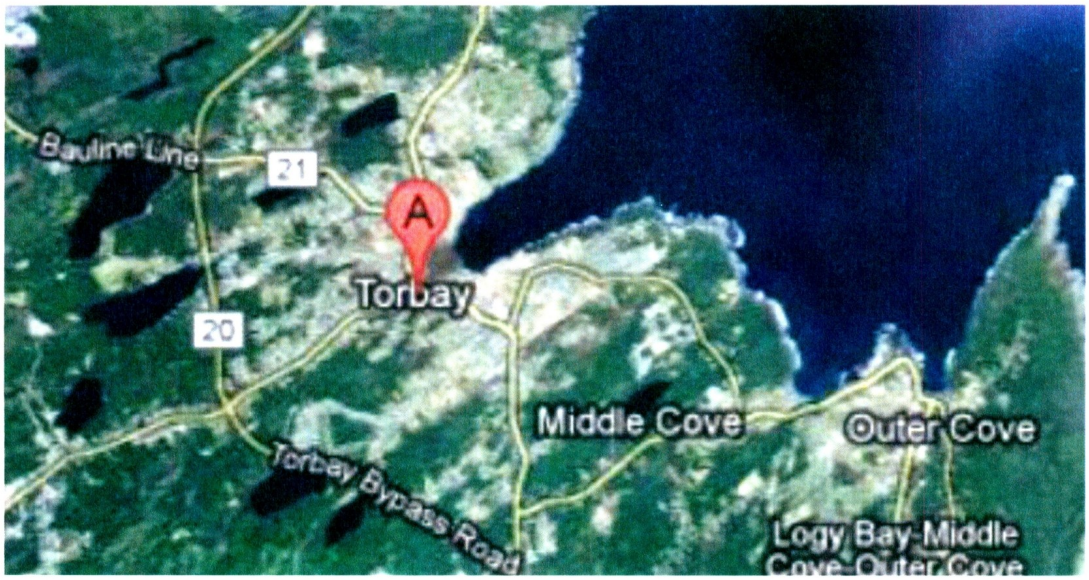

Figure 3-3 Torbay community map

The population of Pouch Cove community is 1,866 and it is located about 30km northeast of St. John's. The main source of raw water is North Three Island Pond and it is chlorinated by gas and the pH is adjusted with Soda ash between 6.5 and 8.5 as per Canadian guidelines.

Figure 3-4 North Three Island Pond Pouch Cove

Figure 3-5 Pouch Cove community map

The above two communities do not have water treatment plants and just rely solely on the chlorination of intake water and pH adjustments.

As discussed earlier, the DBPs are formed by the reaction between the disinfectant dose (residual chlorine) and NOM. Other parameters such as TOC, pH, turbidity and chlorine reaction time also have influence on the formation of DBPs in the drinking water.

Tap water samples from the communities were collected from different locations such as the Post Office, Town Hall and Convenience stores at different times of the day (morning, afternoon and evening) and raw water samples were collected from the intake sources before chlorination. For the preliminary investigations, 5 tap water samples were collected from each location in the month of February. For filtration with activated carbon and clean carbon, 12 time samples were collected in March, April and May. The raw water samples were collected from the intake sources before chlorination, 6 times in months of May and June.

3.1 Sample Collection

All bottles, lids and Teflon liner septa were cleaned with laboratory detergent and washed with tap water and rinsed three times with ultra-pure distilled water for sample collection. The ultra-pure water is highly purified water without minerals and organic matters with high resistance. It is not intended for human and animal uses. It is used in the laboratories and pharmaceutical industries. The tap water samples from the communities of Pouch Cove and Torbay were collected in glass bottles. Before collecting the samples, 100mg of granular ammonium chloride (NH_4Cl) per litre of tap water was added to the sample containers. The purpose of adding NH_4Cl is to convert the free

chlorine residue in the sample to combined chlorine, formed by the reaction of hypochlorite with ammonium ion. Before filling the bottle with tap water, the tap was opened for 3 to 5 minutes to allow for temperature to stabilize. Sample bottles were filled to head space but preventing the flush out of ammonium chloride. The bottles were capped and agitated for 15 seconds after collection. Sample bottles were kept in a chilled container to maintain the temperature below 4°C, and transported to the laboratory within few hours. In the laboratory, the samples were protected from light and kept below 4°C. The collected samples were analyzed within 14 days. The samples extracted were protected from light in glass vials with PTFE-lined caps and stored below -10 °C (Methyl t-Butyl Ether freezing point is -109); extract should be analysed within 10 days.

THMs and HAAs standards were purchased from Sigma-Aldrich (Ontario, Canada) and all column materials were purchased from Fisher Scientific (Ontario, Canada).

3.2 Sample Characterization

3.2.1 Total Organic Carbon (TOC)

TOC was measured with TOC analyzers (Model TOC- 5000A) equipped with infrared detection system. The organic carbon was first converted to carbon dioxide (CO_2), then transferred to the infrared analyzer with the help of a carrier gas, carbon concentration was then determined through CO_2 light adsorption. Dissolved organic carbon (DOC) was determined after passing sample through 0.45μm membrane filter.

TOC was calculated by subtracting inorganic concentration from total carbon concentration as follows:

Total organic Carbon = Total carbon - Inorganic carbon

Table 3.1 TOC Specifications

Measured Object	TC, IC, TOC (TC-IC)
Method	Non-Dispersive infrared Gas Analysis Method
Combustion temperature	680 ^{0}C
Range	4ppb to 4000ppm(4ppb to 5000ppm for IC)
Time for Analysis	2 to 3 minutes for IC and TC (Maximum, 4.5 minutes for TC and 3.5 minutes for IC
Sample injection	Automatic Injector
Carrier GAS	High Purity Air(filled in a cylinder)
Ambient air	5 to 35 ^{0}C

3.2.2 Ultraviolet Absorbance

Ultraviolet (UV) absorbance is based on the principle of measuring absorbance and transmission performance of a given sample. When the beam of light passes through the sample or reflects back from the surface of the sample, it generates broad spectrum of electromagnetic radiation. UV light causes the molecules to change from ground electronic state to an exciting electronic state and therefore electrons shift to higher energy orbits where the electrons dissipate energy in the form of absorbance. The concentration of the sample can be measured by the Beer Lambert Law approach which is

a simple relationship between the absorbance of the occurrence energy or concentration at a particular wave length. It is expressed mathematically as

$$A = \varepsilon b c$$

Where

A = Absorbance of Sample (unit less)

ε = Molar absorptive L/mol-cm

b = cell path length (cm)

c = concentration (mol/L)

Diode Array Spectrophotometer HP 8453UV-Spectroscopy is used for adsorption. This equipment is highly sensitive with a simple optical system. This instrument has a single beam configuration with 1024 diode array elements and produce very high efficiency with very low optical components and range of wavelength is from 190nm to 1100nm.

UV254 analysis was performed on HP 8453 Spectrometer with 1-cm quartz cell. The blank with deionised water was used as baseline before running the sample. The spectrophotometer wavelength was set at 254nm and samples were analysed. Chem station software was used to generate the absorption data and Specific Ultraviolet Absorbance (SUVA) was calculated with the following equation

$$SUVA = UV/DOC*100 \text{ (L/mg-m)}$$

3.2.3 pH

The Model 3000 pH meter was used for pH determination.The buffer solution of pH 4.0, 6.0 and 10.0 with +/- 0.1 sensitivity was used for calibration purposes before measuring pH values.

3.2.4 Turbidity Meter

For measuring turbidity, a 93703 Portable Microprocessor Turbidity Meter was used. It comes with two calibration standards and monthly calibration is recommended.

3.2.5 Free Chlorine

The concentration of free chlorine was measured with HACH pocket colorimeter ll analysis systems using US EPA approved Method 8021(free chlorine) for water, treated water and sea water samples. Method 8167 is used for determination of total chlorine in water, treated water and wastewater. The estimated detection limit (EDL) = is .02 mg/L and the precision at 95% confidence interval = 1+/- .05.

3.2.6 HAA analysis

The micro-electron capture detector (μ-ECD) is used in the GC/ECD and it contains ^{63}Ni radioactive isotopes and generates very high energy beta particles. These beta particles collide with carrier gas molecules and produce a number of new molecules with less energy and each high energy beta particle generates more than 100 low energy particles which are also called free electrons. When interaction between sample molecules and free electrons takes place, the sample molecules capture this free electron and create

the negative ion electron. The pulse function cell electrode collects only the free electron and lets heavier ion go through with carrier gas flow. The function of the pulse rate is to control the cell current and reference current in equilibrium form. To control the reference current, the free electron and the pulse frequency are inversely proportional to each other. When compounds with the free electron go through the cell it produces high pulse rate and low electron concentration. Then this pulse rate changes into voltage and is recorded.

Table 3.2 List of USEPA methods for DBPs MCL guidelines(µg/L)

DBPs	MCL(U.S. EPA)	MCL(Canadian Standard)	U.S. EPA Method
HAAs	60	80	U.S. EPA. 552.3
THMs	80	100	U.S. EPA.501.3

MCL= maximum concentration level

The analysis of HAAs consists of the compounds MCAA, MBAA, DCAA, TCAA, BCAA, BDCAA, DBCAA, DBAA, and TBAA. The Analytical conditions of GC/ µ-ECD are given below.

3.2.6.1 Analytical conditions of GC/ µ-ECD and Method.

Detail of setting GC/ µ-ECD is given below.

Oven Temperature

Initial temperature: 35^0C; Maximum temperature: 325^0C; Initial Time: 9.00 min; Equilibrium temp: 3.00 min

Oven Ramps

Number	Rate	Final Temperature	Final Time
1	1.00	40	3.00
2	6.00	220	10.00
3	0.0		

Post temperature: 250 ^{0}C; Post time: 1.00 min; Run time: 57. 00 min

3.2.6.2 Reagents, Standards and Surrogates

Reagents	Standards	Surrogates
MTBE (Methyl-tert-butyl-ether)	Internal standards 1, 2, 3 Trichloropropane	Surrogate 2, 3 Dibrompropanoic acids
Sodium sulphate		
Sodium Bicarbonate		
Sulphuric acid		
Methanol		
Ultra-pure water		
Ammonium Chloride		
10% Sulphuric acid methanol solution		

3.2.6.3 Calibration

At least five calibration points with concentration ranges of 50, 100, 150, 200 and 250 μL were prepared in ultrapure water. These high concentration values were selected for calibration process because of the higher HAAs concentration in the tap water in the communities being studied. The extraction method is similar to that used for

contaminated water samples as discussed in 4.9.1.Continuous calibration check is required for each batch of sample. The calibration results are as follows.

Table 3.3 HAAs calibration statistics

HAAs compounds	Correlation values r^2
Monochloroacetic acid	99.66
Monobromoacetic acid	99.53
Dichloroacetic acid	99.57
Trichloroacetic acid	99.75
Bromochloroacetic acid	99.36
Bromodichloroacetic acid	99.43
Dibromoacetic acid	99.62
Dibromochloroacetic acid	99.11
Tribromoacetic acid	99.28

3.2.6.4 Extraction Method

Remove sample from the fridge and allow it to equilibrate at room temperature. Pour 40 ml of sample water in a 60 ml glass vial and close with PTFE lined screw cap. Then add 10 µL of surrogate (2.3. Dibromopropanoic acid). To reduce pH values up to .5 or less, add 2mL of H_2SO_4. Immediately after that add 18 gm of muffled sodium sulphate, shake well before it settles. Then add 4mL of MTBE with internal standards, shake briskly for three minute and leave for a few minutes until it develops two layers. With Pasteur glass pipette, move upper layer of MTBE into 15mL conical centrifuge tube. Then add 3mL of 10% sulphuric acid with methanol for each conical centrifugal tube and place in the hot water tub with 50°C temperature for two hours for methylation. Vial should completely submerge in the water up to the compound. Keep the temperature constant at 50^0C throughout this process.

Remove the centrifugal tubes from the tub and wait for a few minutes until they adjust to room temperature. Add 7mL of sodium sulphate solution and vortex three to four times. Wait for a few minutes until it settles down and shows up in two separate layers. Remove the lower phase with Pasteur pipette until .3mL of aqueous remains in the conical tube. Add 1mL of saturated sodium bicarbonate. After first vortex open the cap and allow the release of carbon dioxide from the vial. Vortex three to four times until the neutralization reaction completes. Remove 1mL upper layer from the conical flask and put in to GC-vial. Analyse the sample as early as possible, more detail described at 3.1.

3.2.7 THMs

To measure the concentration of THM compounds in drinking water, the EPA Method 501.3(EPA 500-Series) with purge and trap procedure was used. GC/MS and StratUm PTC were used to measure the THMs values in the drinking water. The Stratum PTC instrument is manufactured to evaluate the volatile organic compounds (VOCs) with the help of a trap and purge procedure. The function of this instrument is to sweep out the VOCs with the help of Helium gas purging from the sealed aqueous sample bottle. When the purged gas passes through the trap, VOCs desorb heat in the trap. Inject the extract into the gas chromatographic detector by back flushing Helium as a carrier gas. The GC/MS separates and detects the individual species. The analytical conditions of GC/MS and Teledyne Tekmar Method are as follows

3.2.7.1 Oven program

Equilibration Time	0.5 min
Max Temperature	260 ^{0}C
Oven temperature	60 ^{0}C for 0 min
	Then 8 ^{0}C /min to 170 ^{0}C
	Post runs time at 260 ^{0}C for 1 min
	Run time 14.75 min

3.2.7.2 Reagents and Standards

Reagents	Standards
Methanol	Fluorobenzene
Ultra-pure water	

3.2.7.3 System Calibration

Five calibration points with concentration values of 1, 10, 40, 60, and 80 µL were prepared in ultrapure water. The extraction method is the same as that used for water sample analysis and is described below.

The calibration results are presented in Table 3.4

Table 3.4 THMs calibration statistics

THMs compounds	Correlation values r^2
Chloroform	99.22
Bromodichloromethane	99.49
Dibromochloromethane,	99.70
Bromoform	99.06

3.2.7.4 Extraction Method

Remove the sample from the fridge and allow equilibration to room temperature. Take 50 ml volumetric flask filled with water sample, spike with 5 µL fluorobenzene, invert the flask three times and pour into the 40 ml glass vial until it is close to overflow (bubble form on the top of the vial) and closed with PTFE lined screw cap. Set the analytical conditions of GC/ MS and Sola tek 72.

Chapter 4 Data Analysis

Tap water collected from Torbay and Pouch Cove was analysed to determine levels of THMs and HAAs at different times of the day. Such analysis contributes to our understanding of the effect of residence time on the formation of these DBPs in the drinking water supply system. In this preliminary analysis, samples were collected in the morning, afternoon and in the evening. The findings of this study are presented in the following sections.

4.1 Variation of HAAs levels in two communities

4.1.1 HAAs in Pouch Cove

As discussed in chapter 1 there are nine main compounds of HAAs. These are Monochloroacetic acid (MCAA), Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), Bromochloroacetic acid (BCAA), Bromodichloroacetic acid BDCAA), Dibromochloroacetic acid (DBCAA), Monobromoacetic acid (MBAA), Dibromoacetic acid (DBAA) , and Tribromoacetic acid (TBAA).

The toxicity of HAAs compounds varies and the relationship between the variations of these compounds within the distribution system at different times of the day were analysed. These results are presented in Table 4.1.The concentrations of all these nine compounds of HAAs are very high except MBAA and TBAA compounds which remain consistently low throughout the day.

As shown, the concentrations of all HAAs were found higher than US EPA and Canadian standards in the water supply system. By closely observing the daily trends, seven compounds of HAAs have been identified in the water supply system. However at noon and in the evening, three compounds in the system reduced to negligible levels but the concentration of four other major compounds (DBAA, BCAA, DCAA and MCAA) were consistently high throughout the day.

As per US EPA regulations, the maximum allowable concentration of MCAA is 70.00µg/L, while the limit for TCAA is 20.00µg/L. Due to high toxicity of MCAA, its level in the drinking water should be very low. There is no published data on BCAA and DBAA. Our analysis demonstrates that these compounds in the drinking water supply system in Pouch Cove are much higher than the US EPA specified limit.

Table 4.1 Concentrations of HAAs in Pouch Cove tap water (µg/L)

Time	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA	EPA THAAs	Canadian THAAs
Morning	58.85	0	91.17	6.67	113.70	30.06	37.58	31.02	0	375.08	60	80
Noon	60.36.	0	104.88	8.57	138.54	37.27	39.85	0	0	451.50	60	80
evening	61.97	0	104.50	6.39	138.14	34.33	37.92	0	0	348.95	60	80
Morning	0	0	64.09	12.18	62.71	44.55	36.31	0	0	254.92	60	80
Noon	30.63	0	59.22	0	63.63	45.62	35.97	0	0	235.07	60	80

The annual total HAAs concentration of all compounds should not exceed more than 60µg/L and 80µg/L according to US EPA and Canadians guidelines respectively. The total concentrations of HAAs in Pouch Cove significantly exceeded both limits.

The one day trend analysis demonstrates that in the evening and at noon time, the concentration of DCAA, BCAA and CDBAA compounds is significantly higher than in the morning (Figure 4.1).

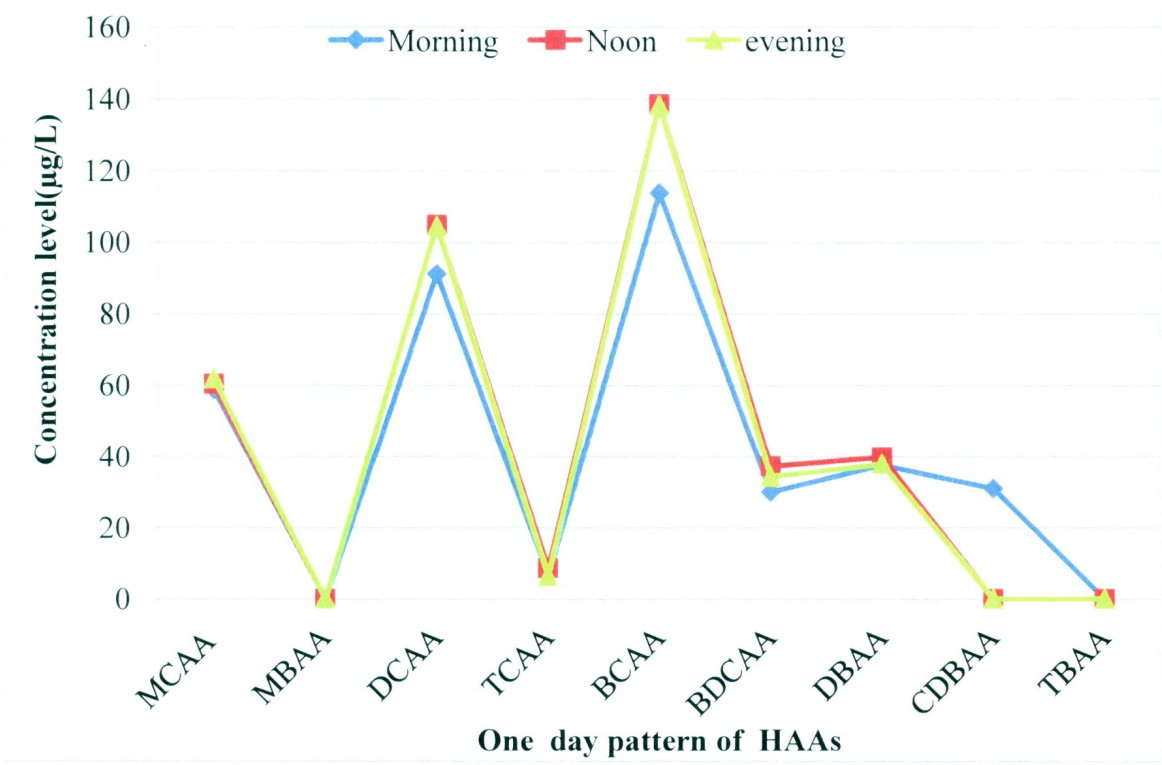

Figure 4-1 Pattern of individual HAA compounds on 24 hour basis

The total concentration of HAAs compounds is high at noon time. The concentration of HAA depends upon the types of microorganisms in the water and their counts, sizes and materials of the pipe and storage tank, sediments in the pipe, NOM, the

disinfectant dose, and treatment technology (Singer et al., 2005; Baribeau et al., 2006). These factors may be one of the causes in the water supply system which allows more time for microbes to react with the free chlorine. Chlorine concentration also decreases because of corrosion, bio-film and scaling in the pipelines (Rossman, 2006; Al-Jasser, 2007) In off-hours of water uses (i.e., from mid night to early morning), due to extra reaction time between the free NOM and free residual chlorine, the level of DBPs in the water increases (Sadiq and Rodriguez, 2004).

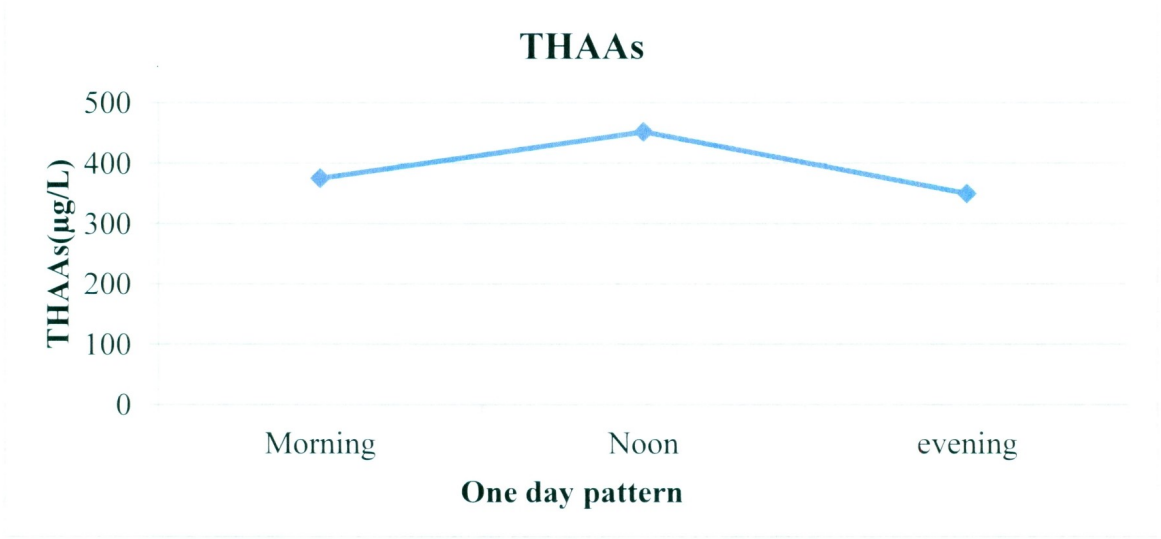

Figure 4-2 Total Haloacetic acid concentration changes in 24 hours

4.1.2 HAAs Levels in Torbay water system

In the community of Torbay, the concentration of all nine compounds of HAAs except MBAA and TBAA is very high throughout the day as shown in (Table 4.2). However the concentration of MCAA, DCAA, BCAA, BDCAA and DBAA is significantly high.

Table 4.2 HAAs in tap waters in Torbay water system (µg/L)

Time	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA	EPA THAAs	Canadian THAAs
Morning	31.02	0	67.18	7.941	80.54	34.77	40.22	53.04	0	314.74	60	80
Noon	39.54	0	61.59	9.33	73.58	38.19	39.21	0	0	261.46	60	80
Morning	0	0	66.80	6.25	56.23	0	35.99	0	0	165.29	60	80
Noon	0	0	58.96	6.25	66.90	34.77	38.01	0	0	204.91	60	80
Evening	27.45	0	56.79	6.00	59.88	0	37.57	0	0	187.72	60	80

The annual total HAAs concentration should not exceed more than 60 and 80 µg/L, according to US EPA and Canadian Guidelines respectively. The total concentration of HAAs in Torbay is much higher than both limits.

The trend analysis shows that in the morning, the concentration of HAAs is higher than the rest of the day. (Figures 4.3).

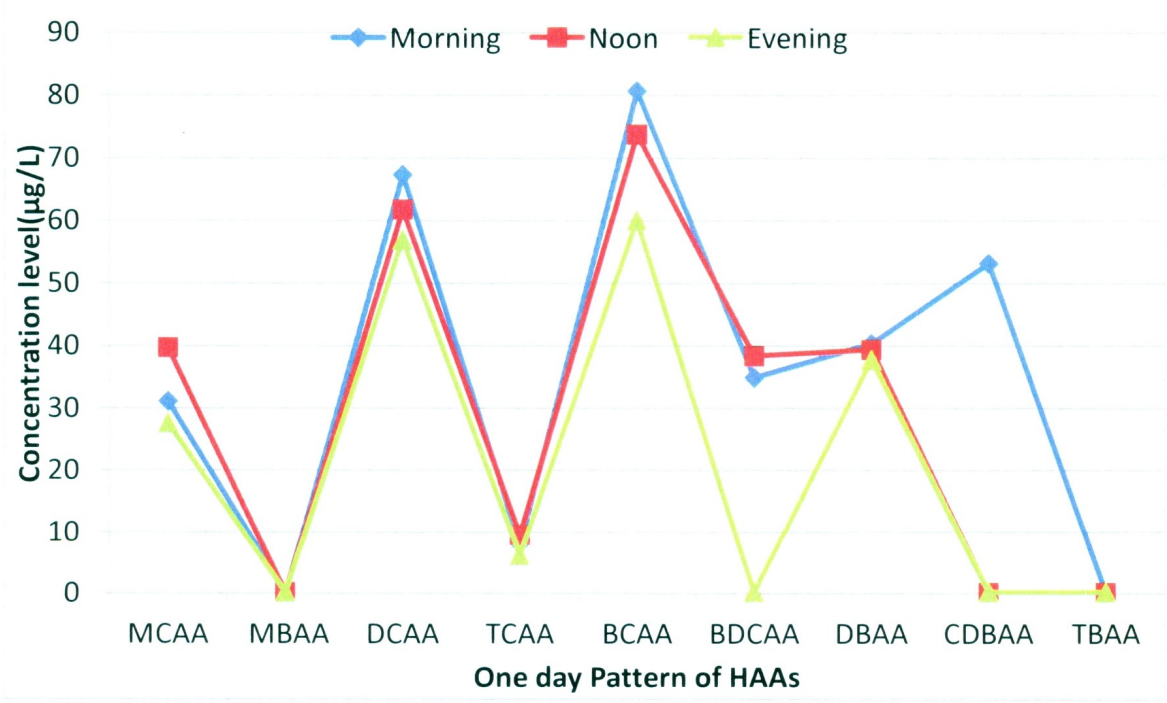

Figure 4-3 Daily trend of HAAs in Torbay community

The concentration of the total HAAs is higher in the morning than other times of the day as shown in Figure 4.4. It may be due to reaction between microbes and free chlorine at night when water use is lowest.

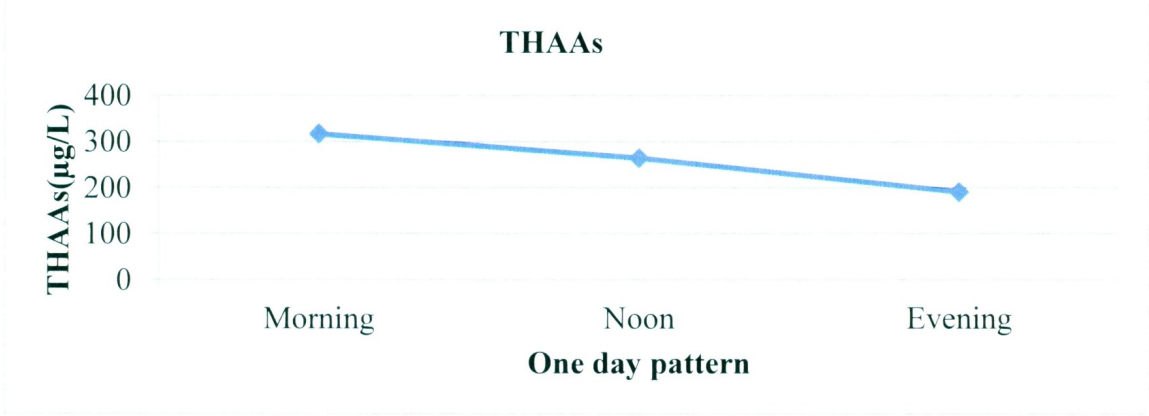

Figure 4-4 Total HAA level in µg/L

4.2 Variation of THM levels in two communities

4.2.1 THM level s in Pouch Cove

The concentration trend of THM compounds is shown in Table 4.3. We observed that chloroform contribution to the total THMs was above 90%, which means that if chloroform is controlled, the total THMs level will be significantly reduced. According to the US EPA recommendations, the concentration of chloroform should be less than or equal to 70 µg/L, DBCM should be less than or equal to 60µg/L but for bromoform and BDCM, there is no published guidelines. These compounds should not exceed these values but the trend shows much higher values for individual THM compounds on daily basis.

Table 4.3 THMs with time in the drinking water- Pouch Cove (µg/L)

Time	Chloroform	BDCM	DBCM	Bromoform	TTHMs
Morning	98.36	3.84	0.29	0.19	102.70
Noon	77.09	3.55	0.25	0.09	81.00
Morning	384.75	3.40	0.19	0.05	388.41
Noon	66.86	5.07	1.23	0.11	72.06
Evening	132.50	9.89	2.10	0.22	144.73

According to the guidelines, the total THMs should not exceed more than 100 µg/L.Table:4.3 illustrate that the total concentrations of THMs are much higher than the limits.

The trend shows that in the morning time, the THM concentration is higher than at other times of the day. Chloroform is the only compound which has the highest concentration throughout the day (Figure 4.5) while other compounds within THMs group are at very low level.

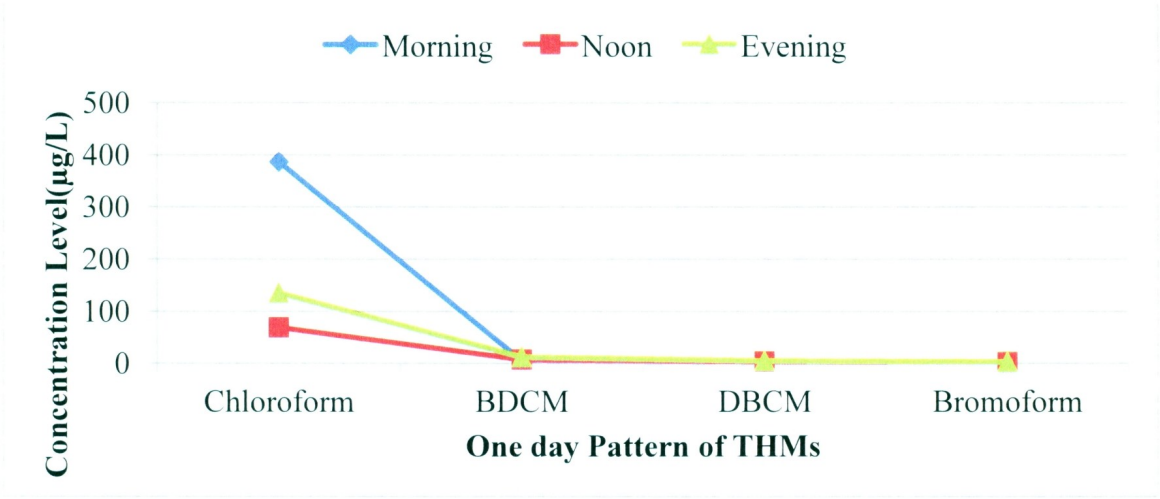

Figure 4-5 Daily pattern of THM in Pouch Cove tap water

The total concentration of THM is much higher in the morning than at other times of the day which is due to reaction of residual chlorine with the NOM in the stagnant water in the system (Figure 4.6).

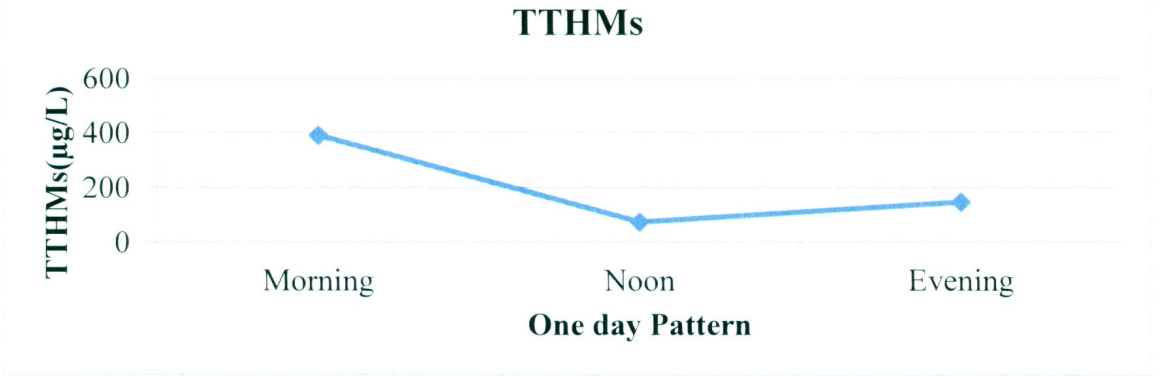

Figure 4-6 Total THM concentration level in Pouch Cove

4.2.2 THM levels in Torbay water system

As shown in Table 5.4, the overall concentration of THMs in Torbay is higher in the morning than other times of the day.

Table 4.4 THMs with time in Torbay community tap water(μg/L)

Time	Chloroform	DCBM	DBCM	Bromoform
Morning	43.47	7.57	1.05	0.04
Noon	43.32	7.60	1.13	0.11
Morning	254.74	35.50	5.88	1.25
Noon	4.34	9.16	0.63	0.12
Evening	45.48	7.37	0.58	0.11

Trend analysis in Figure 4.7 shows that in the morning, the Chloroform concentration is higher than in the rest of the day.

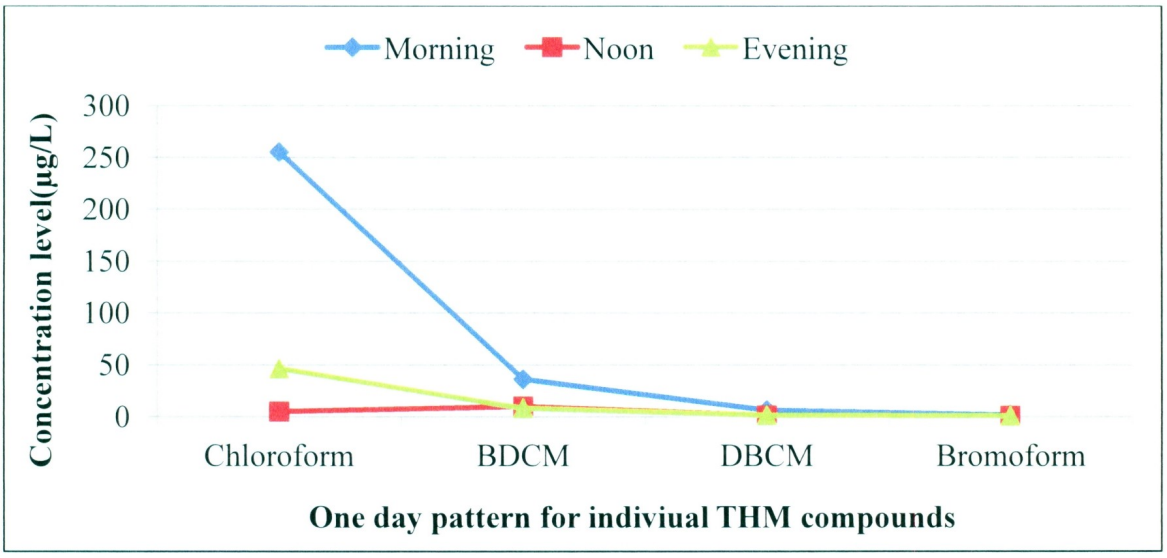

Figure 4-7 Daily pattern for THM concentration in Torbay tap water

The total THMs Concentration is higher in morning time (Figure 4.8)

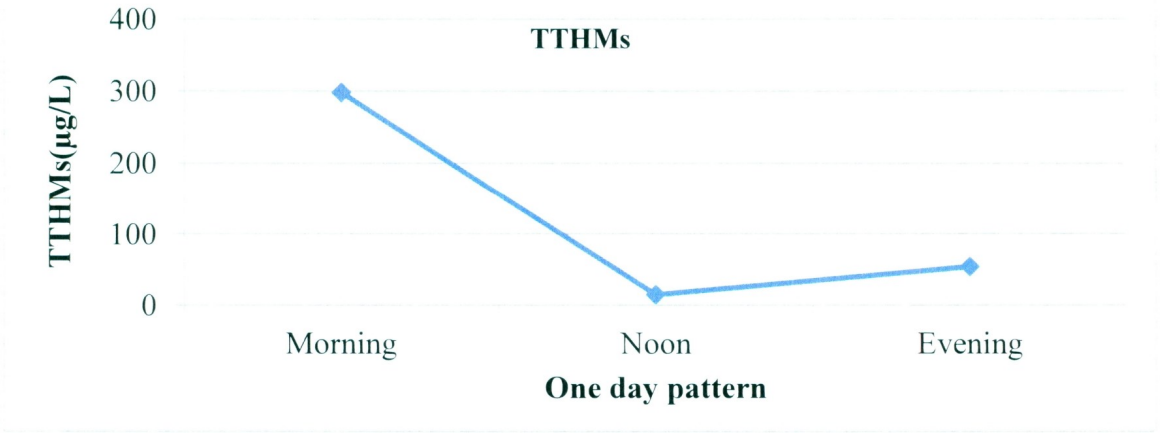

Figure 4-8 Total THM Concentration level in one day

4.3 Comparison of HAA levels in two communities

The levels of HAAs for both communities were compared as shown in Table 4.5. These illustrations demonstrate that the levels of HAAs are much higher in the Pouch Cove community water supply system than in the Torbay water system. In both communities, the concentration levels of HAAs were much higher than the specified US EPA and Canadian guidelines.

Table 4.5 Total HAAs in two communities (µg/L)

	Pouch Cove	Torbay		
TIME	THAAs	THAAs	EPA THAAs	Canadian THAAs
Morning	375.08	314.74	60	80
Noon	451.50	204.91	60	80
Evening	348.95	187.72	60	80

As shown in Table 4.6, both communities have high concentration of total THMs, exceeding the guidelines. At noon and in the evening times, the total THMs in the Torbay water supply system is lower than the Canadian guideline, but in Pouch Cove, the levels are much higher in the morning and evening times than at noon time.

Table 4.6 Total concentration of THMs in two communities

	Pouch Cove	Torbay		
Time	TTHMs	TTHMs	EPA TTHMs	Canadian TTHMs
Morning	388.41	297.39	80	100
Noon	72.06	14.27	80	100
Evening	144.73	53.55	80	100

Chapter 5 Reduction of HAAs and THMs

5.1 Flask Testing

The analysis of tap water from the two communities indicates that the mean HAAs and THMs were found higher than the acceptable limits as outlined by the Health Canada. To reduce the concentration of these compounds to an acceptable levels, a series of experiments using activated carbon with batch and column tests were conducted. For each test, 15 gm activated carbon extracted from heavy oil fly ash was used.

This section covers batch test using activated carbon. The finding reported in the beginning of the previous chapter will provide valuable data to assist in controlling DBPs in the drinking water. In order to reduce the total organic carbon in the intake water sources, which is the main precursor in the formation of DBPs, a separate test was conducted. The results of removal efficiency of TOCs will be discussed later in this chapter.

5.1.1 Material and Methods

In this study, carbon extracted from heavy oil fly ash (HOFA) was used as a filter media. HOFA was collected directly from the electrostatic precipitator of the power plants which use heavy fuel oil as a fuel source. The impurities from HOFA were removed using the following cleaning procedures.

1. HOFA was washed with distilled water with the ratio of 1gm of fly ash with 10 ml of water and stirred at 10 rpm using Birds & Philips stirred Model number 7790-400 for 12 hours with the magnetic bar dip in the solution, at room temperature.

2. After filtration, the washed raw HOFA was thoroughly mixed with aqueous acid solution in the ratio of 1gm of fly ash with 5 ml distilled water, with 28% nitric acid solution at 60°C for 2 hours and then rinsed with the distilled water to remove nitrate ions.

3. The nitric acid washed HOFA was then treated with HCL in the ratio of 1gm of fly ash with 5 ml distilled water with 15% HCL at 60°C for one hour and rinsed with the distilled water to remove the chloride ions.

4. After washing, the wet clean carbon was dried in the oven for 24 hours at 105 °C.

5. After completion of the washing process a programmable Lindberg/Blue M tube furnace was used for the activated carbon process. The furnace temperature was programmed up to 900°C with increment of 5°C/ min and then remained at this 900°C temperature for 30 to 60 minutes. During this period the constant flow rate of the ultra-pure compressed air and nitrogen was set to 5ml/min (Mofarrah et al., 2012)

6. At the end, the treated washed fly ash converted into activated carbon.

A detailed analysis was conducted for raw fly ash and treated carbon for heavy metals as listed in Table 5.1.

Table 5.1 Metals in heavy oil fly ash (HOFA)

Metal (mg/kg)	Raw HOFA(mg/kg)	Washed HOFA(mg/kg)
Arsenic(As)	ND	ND
Cadmium(Cd)	ND	ND
Cobalts(Co)	1.23	ND
Chromimum(Cr)	12.03	7.73
Copper(Cu)	3.6	ND
Mercury(Hg)	.094	ND
Nickle(Ni)	2176.32	331.91
Lead (Pb)	2.593	ND
Selenium (Se)	ND	ND
Vanadium(V)	5251.471	221.321
Zinc(Zn)	46.947	14.858
Carbon	86.12%	89.65%

ND = Not detectable

As shown in figure 5.1 the particle size of HOFA was measured with the HORBIA PARTICLE laser scattered particles size analyzer model LA-950 with wet dispersion methods in $NAPO_3$ solution. It shows the mean diameter of the collected washed fly ash is 59.39.5μm with standard deviation 31.54 μm.

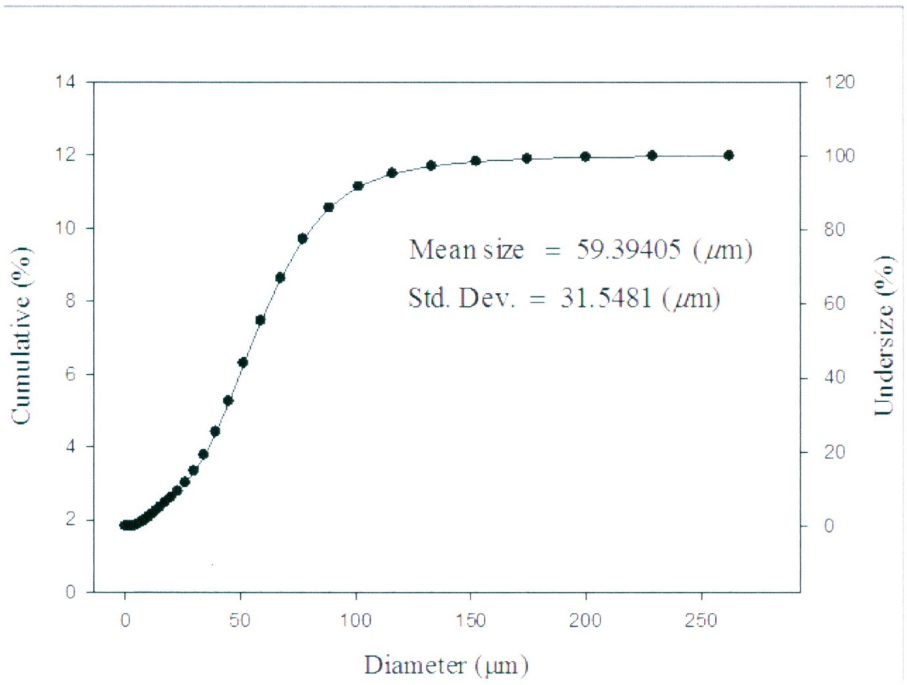

Figure 5-1 Particle size graph

5.1.2 Adsorption in Flask Experiments.

The objective of this experiment was to assess the removal of THMS and HAAs from the drinking water using activated carbon. The 2^3 design parameters considered for this experiment included activated carbon dose, temperature, and pH values (Montgomery, 1997).

To evaluate the removal efficiency of THMs and HAAs from the tap water collected from the Pouch Cove community, batch test was conducted by taking different doses of AC samples in 125 mL of tap water with known initial concentrations of THMs and HAAs. To run the experiment in batch mode, 125mL of water was taken in eight 250mL Erlenmeyer flasks and AC was added with ratio as shown in Table 5.2 and was

agitated with magnetic stirrer at the 10 rpm for 24 hours. To avoid the evaporation of water from the flask it was sealed with a stopper. To reduce the pH value of contaminated water, sulfuric acid of a known concentration and amount was added to obtain a desired value of pH as listed in Table 5.2. In Table 5.3 range and levels (coded as -1 and+1) were designed for selected variables that play a major role in the adsorption processes. The percentage removal of THMs and HAAs was calculated on the basis of initial and final concentration of THMs and HAAs using the formula $R = \frac{[C_0 - Cf] * 100}{C_0}$ as shown in Table 5.4 where C_0 is reference tap water concentration and C_f is the concentration in the water after flask test.

Table 5.2 Design parameters

Sample name	Coded values			Actual		
	A	B	C	Temperatures °C	Activated carbon(gm)	pH
B1	-	-	-	22	1	2
B2	+	-	-	30	1	2
B3	-	+	-	22	2	2
B4	+	+	-	30	2	2
B5	-	-	+	22	1	6.6
B6	+	-	+	30	1	6.6
B7	-	+	+	22	2	6.6
B8	+	+	+	30	2	6.6

Table 5.3 Experimental design of the batch test

Variables	Factor	Coded Level	
		-	+
AC dose(mg)	A	1	2
Temperature	B	22	30
pH	C	2	6.6

HAA Removal

The removal efficiency of HAAs after batch test is shown below in Table 5.4. Review of the data shows that the highest removal of HAAs occurred when the temperature and pH values were low and activated carbon is in high dose. The removal efficiency was 35.56%. For experimental design and to optimize parameters, Design Expert Software version 8.07 was used (Design Expert, 2012).

The analysis of variance (ANOVA) shows that the results were significant for $p<.05$, which means that there is a significant effect on the removal of HAAs from the given batch test; in this case activated carbon and interactions of temperature and pH have significant effects with correlation co-efficient $R^2=.9646$ The main effect of the adsorption of HAAs on each parameters analysis is listed in Table 5.4 which shows the sensitivity analysis and Figure 5.5 shows the contribution of different parameters. The

regression relationship of HAAs removal with various combinations of parameters was developed as listed in Equation 5.1 below.

% HAAs removal = +32.82 - .41 x A+1.05x B-0.58 x C+1.0 x A x C (5.1)

Where A, B, and C are temperatue, activated carbon dose, and pH respectively. Equation 5.2 below shows % HAAs removal in term of actual code factors.

% HAAs removal = +32.82 - .41 x temperature + 1.05 x activated carbon - .58 x pH + 1.0 x temperature x pH (5.2)

Table 5.4 Experimental data and percentage removal of HAAs

A: Temperature, B: Activated Carbon C: pH

Sample name	Coded values			Actual			% HAAs Removal
	A	B	C	Temperatures °C	Activated carbon(gm)	pH	
B1	-	-	-	22	1	2	34.59
B2	+	-	-	30	1	2	33.10
B3	-	+	-	22	2	2	35.56
B4	+	+	-	30	2	2	30.77
B5	-	-	+	22	1	6.6	30.77
B6	+	-	+	30	1	6.6	31.38
B7	-	+	+	22	2	6.6	32.4
B8	+	+	+	30	2	6.6	34.40

Table 5.5 Contribution of different parameters on removal of HAAs

A: Temperature, B: Activated Carbon C: pH

Parameters	% Contribution for HAAS adsorption
A- Temp	5.83
B-activated carbon	38.96
C-pH	11.96
Effects of A x C	39.68

In Figure 5.2 the pareto chart shows that factor B (activated carbon) has a significant effect on HAAs removals. The interactions between factor C (pH) and factor A(temperature) also have a significant effect on HAAs removal.

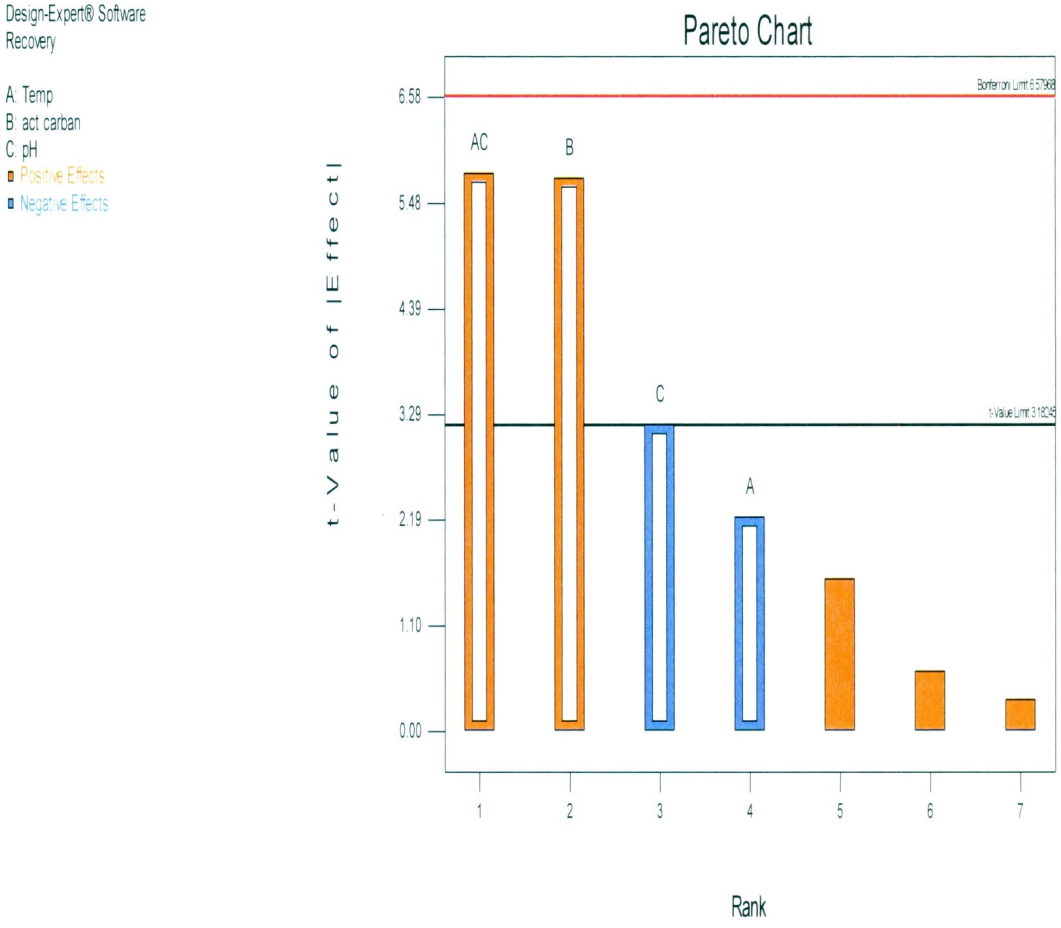

Figure 5-2 Pareto chart for HAAs

THM Removal

The percentage of THM removal by batch test is shown in the Table 5.6. As demonstrated in the table, the activated carbon dose at B4 shows the highest removal percentage of THMs (95.56%) when considering the factor of temperature factor and activated carbon dose on higher side and pH on lower end, B1 and B5 show very little recovery. Analysis of variance (ANOVA) shows significant correlation ($p < .05$) on the

removal of THMs from the given batch test. In this case parameters are amount of activated carbon used and temperature variations. These two parameters have significant effect on the removal of THMs with correlation co-efficient R^2 as 0.90.The main effect of each parameter on the analysis of THMs adsorption is provided in Table 5.7. The following regression relationship is developed to predict % THM removal:

$$\%THMs\ remove = 4.64+69.01 \times A + 87.23 \times B - 66.00AB \qquad (5.3)$$

Where A, B and C shows temperatue , activated carbon and pH respectively.

Table 5.6 Experimental data and percentage removal of THMs

A: Temperature, B: Activated Carbon C: pH

Sample name	Coded values			Actual			% THMs Recovery
	A	B	C	Temperature °C	Activated carbon(gm)	pH	
B1	-	-	-	22	1	2	94.29
B2	+	-	-	30	1	2	6.51
B3	-	+	-	22	2	2	89.90
B4	+	+	-	30	2	2	95.56
B5	-	-	+	22	1	6.6	44.90
B6	+	-	+	30	1	6.6	94.06
B7	-	+	+	22	2	6.6	87.80
B8	+	+	+	30	2	6.6	92.69

Table 5.7 Contribution of different parameters on removal of THMs

Parameters	% Contribution for THMs adsorption
A- Temp	25.63
B - activated carbon	40.95
C-pH	0.18
A x B	23.44

In Figure.5.3, the pareto chart shows that factors B (activated carbon) and factor A (temperature) have significant effects on THMs removal.

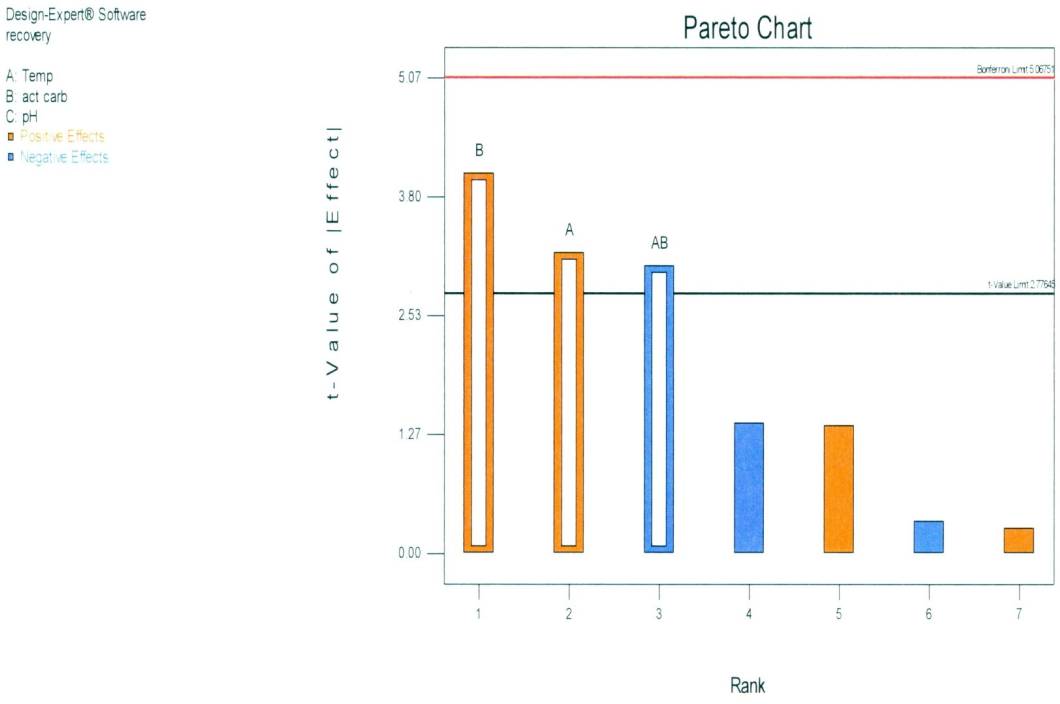

Figure 5-3 Pareto chart for THMs

5.2 Column Testing

Column test experiment was designed using Pyrex glass column with dimension of 30 cm length and 40 mm internal diameter. The experiment setup is shown in Figure 5.4, 15 mg of activated carbon was used in the column. In order to prevent leaching of the fine particles into filtered water, glass wool and a 1μm filter at the outlet of the column

were used. The column test was conducted using the same tap water which was used in the batch test. A flow rate of 3.5 ml/min was maintained using a peristaltic pump. The advantage of using a peristaltic pump is that there is no cross-contamination since flowing water through the column does not touch any mechanical part of the pump and water passes through the internal tubing system. The filtered sample was collected and analysed for the concentration of THMs and HAAs in the Torbay and Pouch Cove communities.

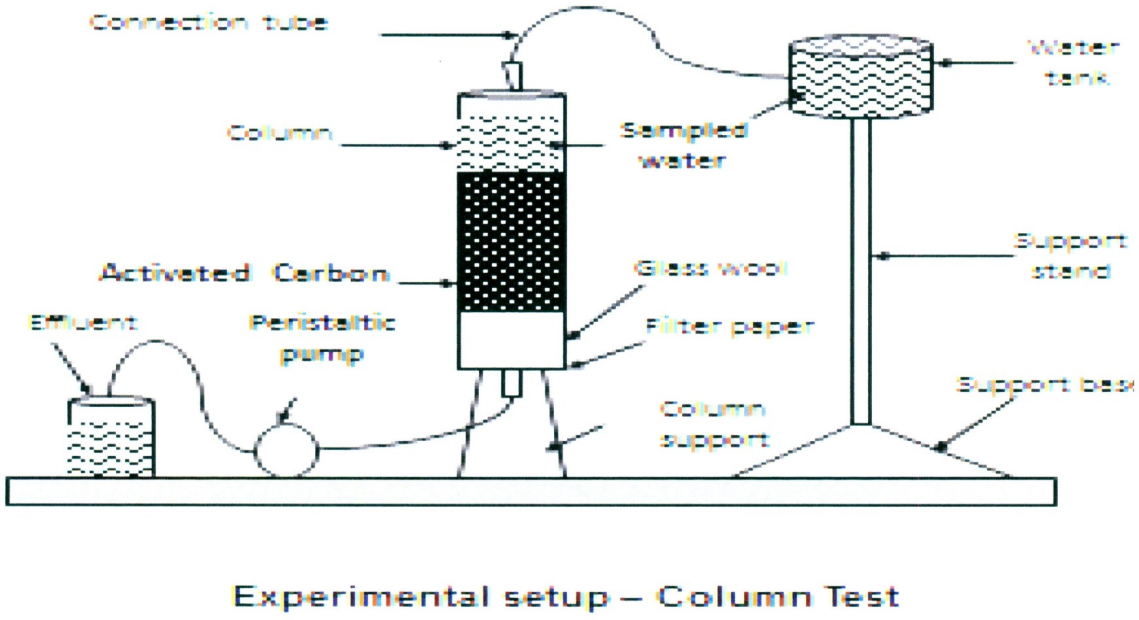

Figure 5-4 Column test setup

5.3 THM removal through Activated Carbon

5.3.1 THM removal from tap water in Pouch Cove

The tap water collected from Pouch Cove was analysed to determine the level of THMs and HAAs after filtration. The results are tabulated in Table 5.8. The individual compound concentration values before and after filtration are listed. It is obvious that the chloroform concentration was 46.14μg/L, while the total THMs was 61.81μg/L. It shows that out of four compounds in THM group, chloroform was more than 70% of the total THMs in the tap water before filtration.

The concentration of BDCM was 4.42μg/L, a significant amount of chloroform and BDCM was removed through filtration process. There was no significant removal of DBCM and Bromoform from the tap water. The total THM in the tap water after 740 minutes of filtration was only 46.18μg/L which is still below the reference concentration, as compared to other compounds. As shown in Table 5.8, the reference tap water has total THMs of 60.81 μg/L before filtration but after continuous filtration with activated carbon for 740 minutes its total concentration did not reach its initial concentration. After filtration for 260 minutes the filtration media was saturated and the efficiency declined.

Table 5.8 THMs compounds in Pouch Cove Tap water before and after filtration (all values in µg/L)

Time (minute)	Chloroform	BDCM	DBCM	Bromoform	TTHMs	C_o/Ci
Tap water before filtration	46.14.	4.42	4.40	5.83	60.81	1
Filtered water (20)	5.23.	0	4.17	5.39	14.80	0.24
40	12.59.	2.40	4.16	5.24	24.40	0.40
60	14.36	2.76	4.18	5.23	26.55	0.43
80	24.91.	0	4.17	5.23	34.32	0.56
100	26.76	0	4.28	5.23	36.28	0.59
120	27.33	0	4.18	5.24	36.76	0.60
140	40.60	3.69	4.19	5.23	53.73	0.88
260	28.60	6.64	4.20	5.24	44.80	0.73
380	26.44	6.08	4.24	5.45	42.68	0.70
500	25.32	5.93	4.21	5.44	40.53	0.66
620	33.09	6.26	4.18	5.58	49.28	0.81
740	30.18	6.27	4.22	5.48	46.40	0.76

Figure 5.5 shows variation of total THMs with respect to time of filtration and Figure 5.6 shows a breakthrough curve drawn between relative concentration (C_0/C_i) and filtration time. It can be seen that the filtered water concentration gradually increased with time but its concentration is below 60% of the raw water concentration. Here C_0 is filtered water THM concentration and C_i is the raw water THM concentration. This plot shows how filtered water concentration reached the initial raw water concentration (US. Army Corps Engineer, 2001). In the filtration process 50% of the raw water concentration in the

filtered water is considered as the breakthrough point (Yong et al., 1992; Shackelford et al., 1993).

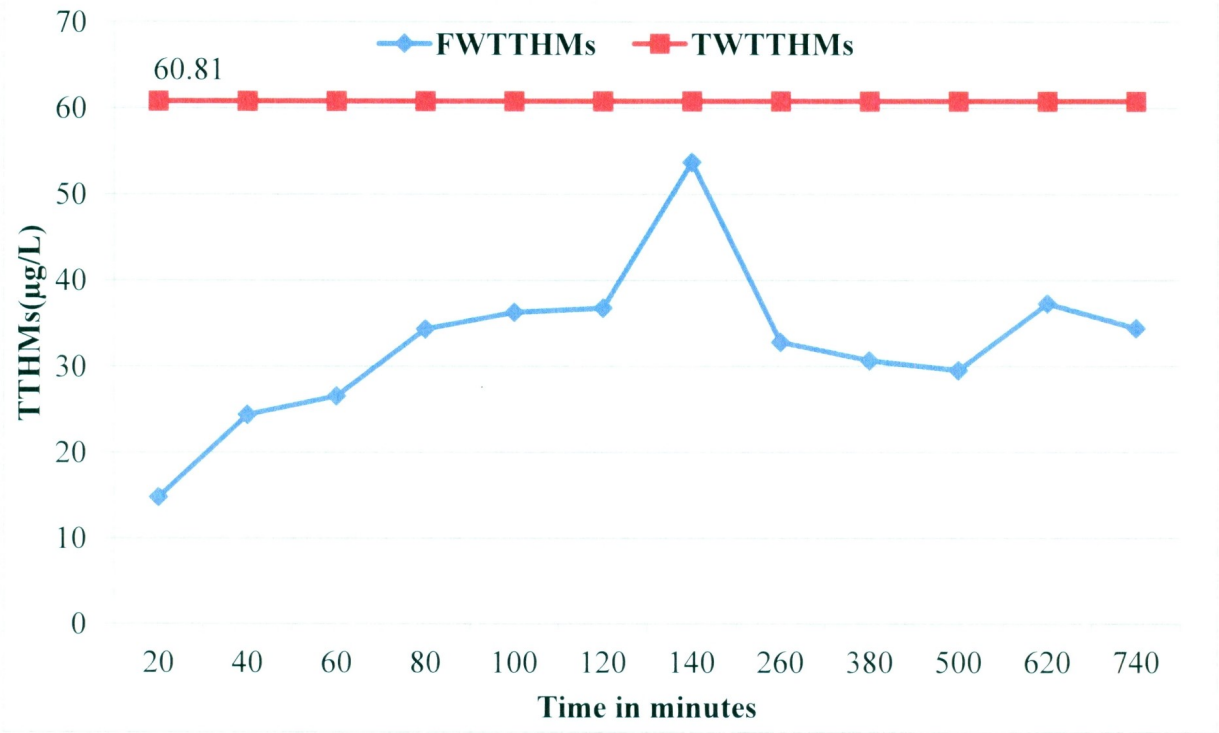

Figure 5-5 TTHM concentration with filtration time

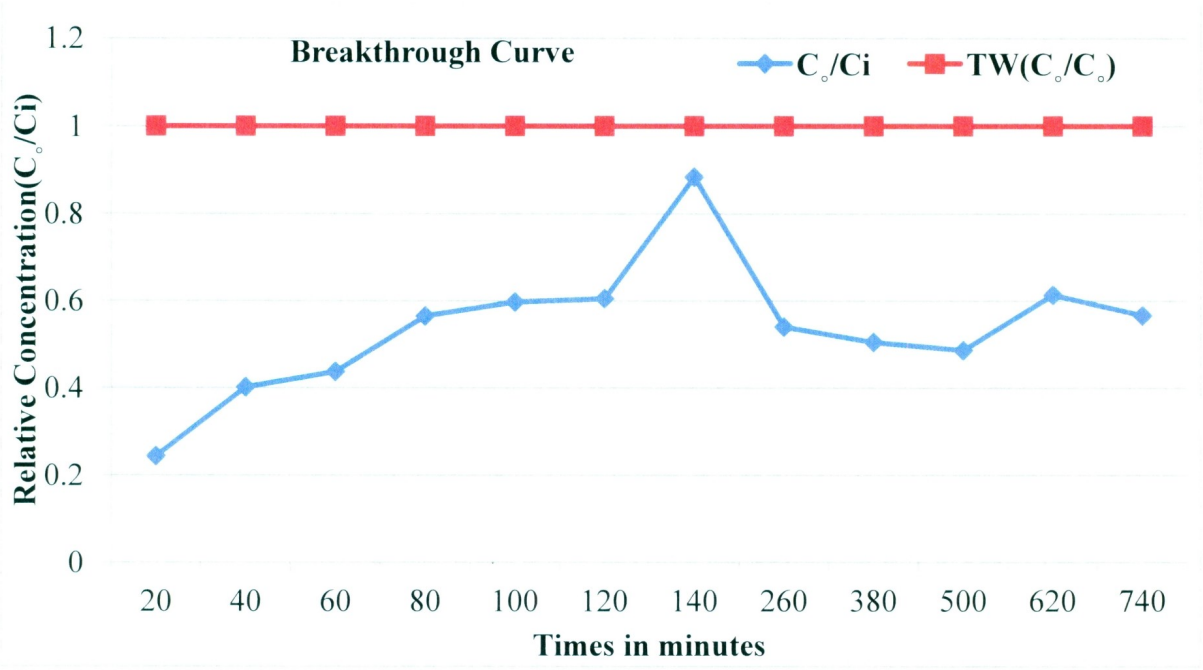

Figure 5-6 Relative concentration (C_0/C_i) with time

5.3.2 THM removal from tap water in Torbay

We observed that the trend of the Torbay water system filtration with the adsorbent was found very effective in the removal of chloroform as shown in Table 5.9. The chloroform in the raw water was 259.36µg/L which after filtration for 740 minutes, was reduced to 56.06µg/L. The initial concentration of other compounds such as BDCM was 38.41µg/L and was reduced to 5.17µg/. This indicates that the activated carbon is very effective on the removal of these two THM compounds. The level of reduction for other two compounds such as DBCM and bromoform was not significant.

Table 5.9 Individual THM compounds in unfiltered and filtered water in Torbay community

TIME (minute)	Chloroform	BDCM	DBCM	Bromoform	TTHMs	C_o/Ci
Tap water before filtration	259.36	38.41	10.39	12.47	320.65	1
Filtered water 20	5.43	0	4.16	5.23	14.84	0.04
40	0	2.41	4.16	5.23	11.42	0.03
60	4.20	2.720	4.18	5.23	16.34	0.05
80	194.43	32.42	5.66	8.59	241.12	0.75
100	13.01	4.51	4.79	5.24	27.56	0.08
120	101.57	20.24	5.94	5.30	133.06	0.41
140	8.1	4.70	4.58	5.23	22.34	0.04
260	63.62	5.31	4.30	5.23	78.47	0.24
380	65.77	4.87	4.33	5.68	80.66	0.25
500	5.57	5.62	4.33	5.30	20.83	0.06
620	58.01	4.57	4.25	5.50	72.36	0.22
740	56.06	5.17	4.30	5.35	70.90	0.22

As shown in Figure 5.7 reference tap water has a total THM concentration of 332.24μg/L before filtration. However after continuous filtration through activated carbon for 740 minutes, its total THM concentration was on average less than 50 μg/L, which indicates that the filtration is very effective in removing chloroform and BDCM because these two compounds are dominant. As shown in the Figure 5.8, trend shows that the filtered water THMs concentration gradually increased, due to saturation. But it is much below the level in the unfiltered water even after 740 minutes of filtration.

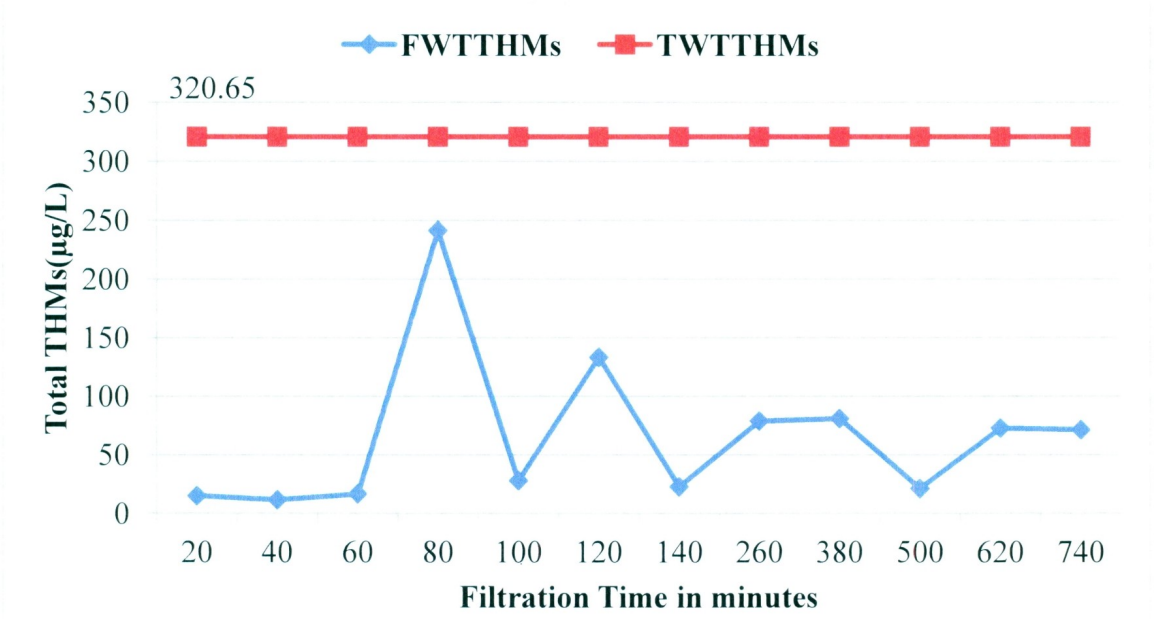

Figure 5-7 Total THM variation with time in filtered water in Torbay community

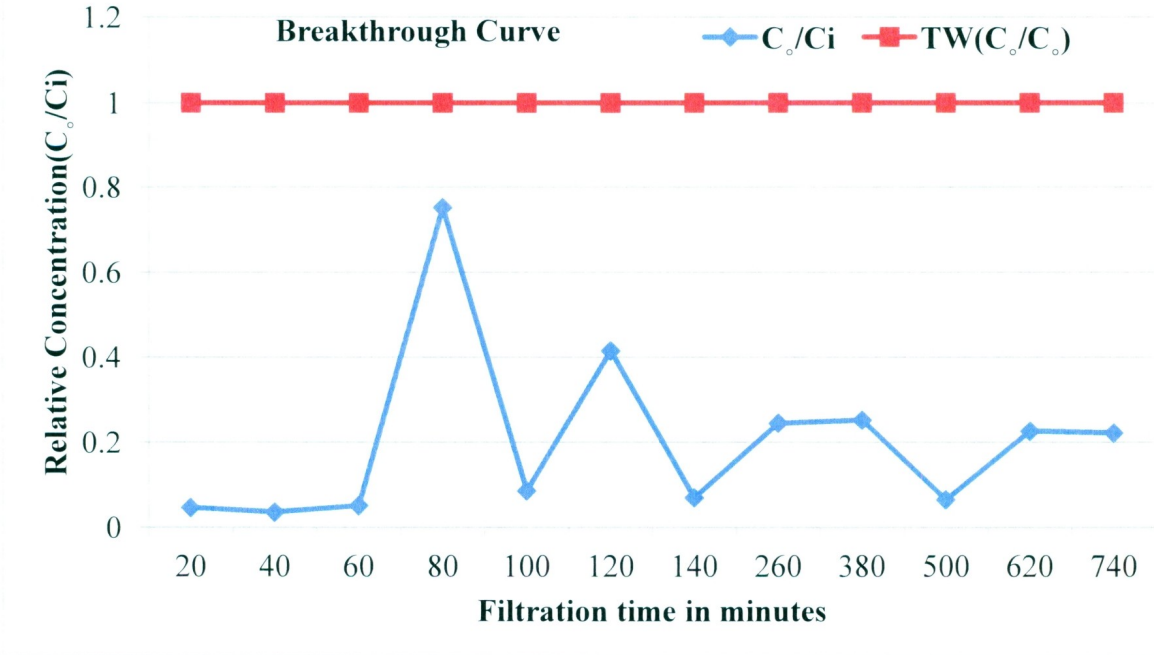

Figure 5-8 THM variation with time in Torbay communi

5.4 HAA removal through using activated carbon

5.4.1 HAA removal from tap water in Pouch Cove Water

The filtration media adsorption did not have much effect on the removal of all HAAs compounds. It is only effective in the removal of BCAA. As shown in Table 5.10 the initial concentration is very low after 40 minutes of filtration but concentration starts increasing after 40 minutes of continuous filtration. At 260 minutes, the concentration in the filtered water was similar to the raw water concentration, which indicates that the filtration medium does not have much impact on the removal of HAA compounds. However after 500 minutes of filtration, media was fully saturated and started releasing HAA with raw water.

Table 5.10 Individual HAA compounds in tap water before and after filtration in Pouch cove community (µg/L)

Time (minute)	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAAs	C_o/C_i
Tap water before filtration	0	0	75.23	5.70	77.12	0	36.54	0	29.12	223.72	1
Filtered water(20)	0	0	69.48	4.69	38.88	0	0	0	0	113.06	0.50
40	0	0	78.47	5.64	74.76	0	36.14	0	0	195.03	0.87
60	0	0	70.75	5.44	76.67	0	36.29	0	0	188.71	0.87
80	0	0	67.74	5.25	76.41	0	36.28	0	0	174.00	0.77
100	0	0	63.12	5.05	69.69	0	36.12	0	0	173.06	0.77
120	0	0	73.00	5.47	80.02	0	36.56	0	0	195.06	0.87
140	0	0	69.18	5.19	73.92	0	36.28	0	0	184.5	0.82
260	0	0	114.37	86.32	16.24	0	1.63	0	0	218.56	0.97
380	0	0	108.49	118.18	15.82	0	1.62	0	0	244.13	1.09
500	0	0	133.33	134.40	16.66	0	1.64	0	0	286.05	1.27
620	0	0	111.6671	115.90	15.83	0	1.62	0	0	245.03	1.09
740	0	0	111.44	122.46	16.02	0	1.61	0	0	251.54	1.12

Figure 5.9 and Figure 5.10 demonstrates the trend with the time of filtration.

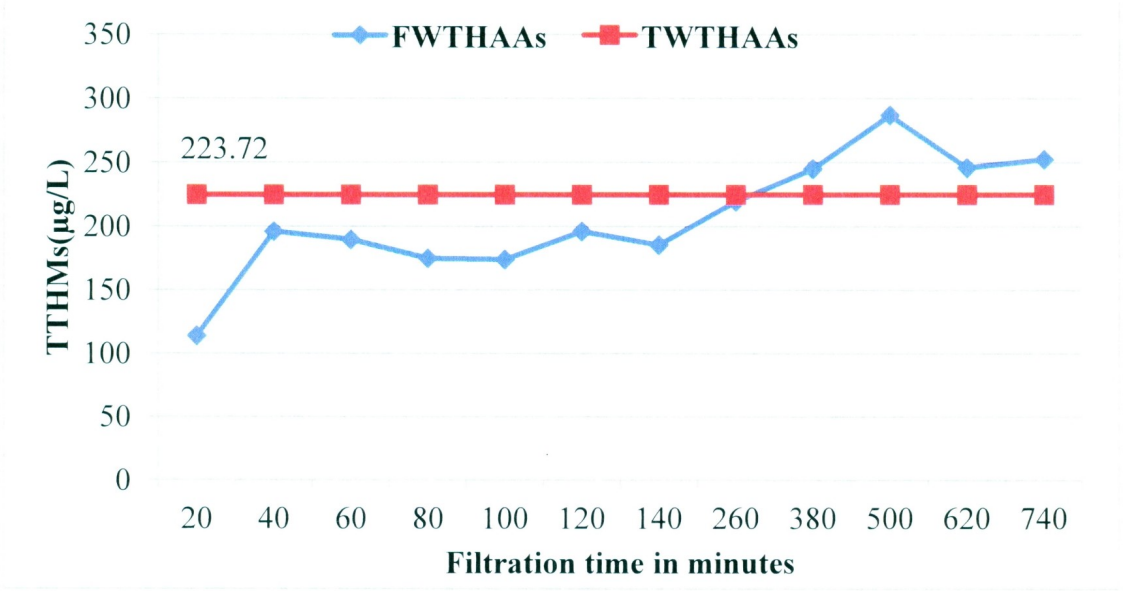

Figure 5-9 Graph between Time and TTHMs concentration

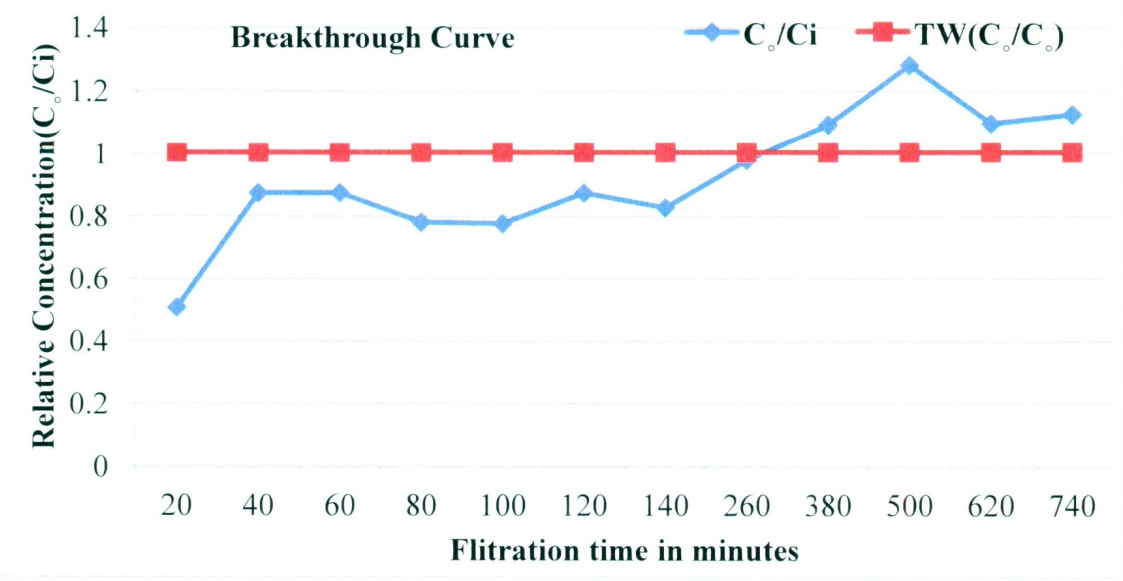

Figure 5-10 Relative concentration (C_0/C i) trend with time of filtration

5.4.2 HAA removal from tap water in Torbay Water

The adsorbent does not have much effect on the removal of HAA compounds from Torbay water supply system (Table-5.11). The initial and final concentration of HAA compounds are equivalent after 20 minute.

Table 5.11 HAAs in tap water before and after filtration in Torbay community (µg/L)

Time (minute)	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA	C_o/Ci
Tap water before filtration	0	0	51.01	5.48	48.71	0	36.39	0	0	141.60	1
Filtered water(20)	0	0	55.06	0	32.53	0	0	0	0	87.59	0.61
40	0	0	59.46	6.06	51.68	0	35.80	0	0	153.02	1.08
60	0	0	50.73	5.41	52.30	0	36.60	0	0	145.06	1.02
80	0	0	48.26	5.32	46.34	0	36.39	0	0	136.32	0.96
100	0	0	0	5.98	54.61	0	37.23	0	0	97.83	0.69
120	0	0	52.88	5.69	52.07	0	35.27	0	0	145.92	1.03
140	0	0	50.31	5.52	45.23	0	36.14	0	0	137.21	0.96
260	0	0	61.02	66.98	15.94	0	1.76	0	0	145.72	1.02
380	0	0	57.57	64.89	16.24	0	1.78	0	0	140.50	0.99
500	0	0	62.75	68.82	17.03	0	1.82	0	0	150.44	1.06
620	0	0	59.79	69.86	16.75	0	1.78	0	0	148.20	1.04
740	0	0	61.48	66.21	16.50	0	1.78	0	0	145.99	1.03

As shown in Figure 5.11 and Figure 5.12 the trend shows that after 20 minutes the filtration media was saturated.

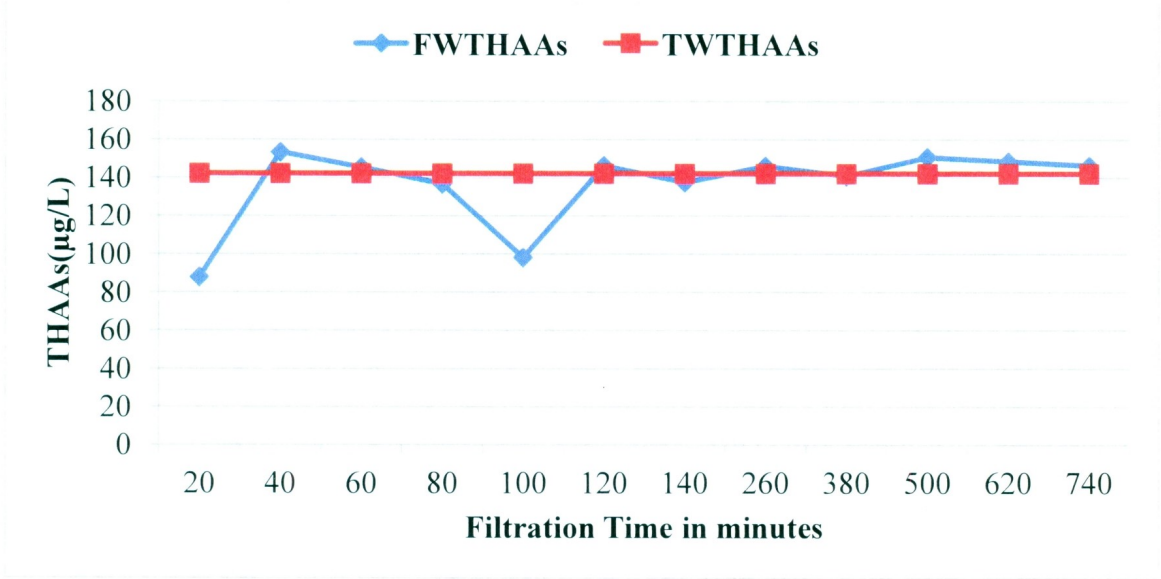

Figure 5-11 Graph between Time and THAAs concentration

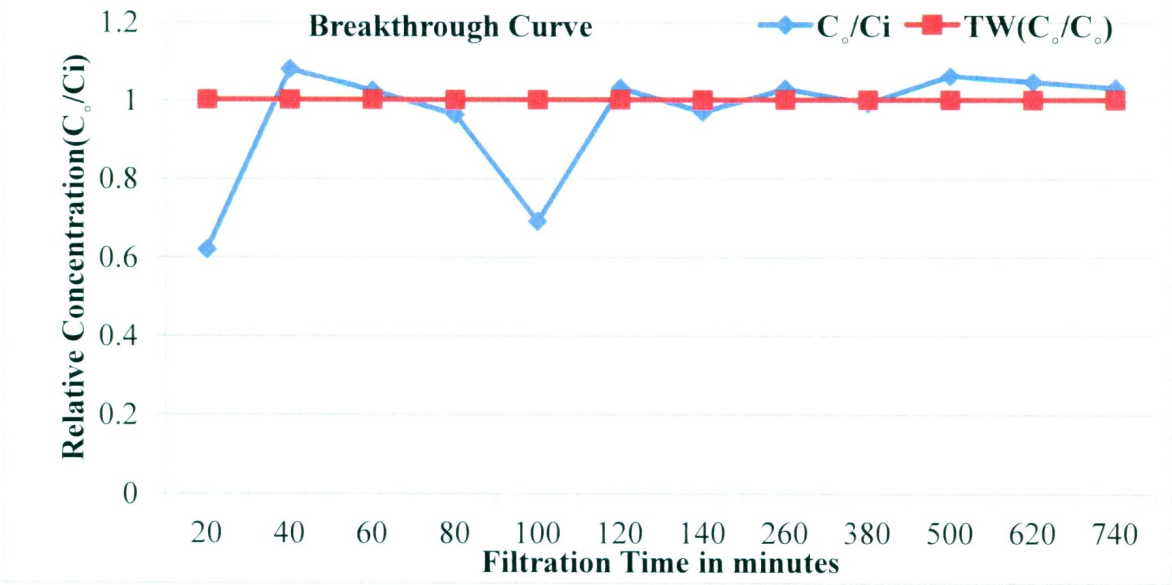

Figure 5-12 Relative concentration (C_0/C_i) trend with time of filtration

5.5 THM removal through using clean carbon

5.5.1 THM removal from tap water in Pouch Cove

After using activated carbon in phase first, clean carbon without activation was used in phase two as an adsorbent for the Pouch Cove and Torbay water supply systems. The purpose was to compare removal efficiency by two types of carbon (with and without activation). The results are very encouraging to remove chloroform, BDCM, and bromoform. As compared to the activated carbon, the adsorbent used in this experiment helped in significant removal of THMs while activated carbon was effective in removing chloroform only. As shown in Table 5.12 chloroform has a concentration of 219µg/L in the total THMs in the reference tap water. While running water through filter media for 1440 minutes, the concentration of the total THM was reduced to 70.12µg/L. After 2880 minutes of filtration, the concentration of chloroform reduced by 50%. BDCM constitutes 27.45µg/L in the total THMs concentration, but after 1440 minutes of filtration, the concentration of BDCM reduced to half of the reference water concentration. The bromoform concentration in the reference water was 22.28µg/L but after filtration it shows zero concentration in the filtered water. Only DBCM percentage contribution remained unchanged in the whole process.

Table 5.12 THM compounds in tap water before and after filtration in Pouch Cove community (µg/L)

Time(minute)	Chloroform	BDCM	DBCM	Bromoform	TTHMs	C_o/C_i
Tap water before filtration	219	27.45	19.86	22.25	288.57	1
30	0	15.84	20.63	0	36.48	0.12
60	0	14.75	19.67	0	34.42	0.11
120	0	15.54	20.21	0	35.76	0.12
180	0	14.75	19.59	0	34.35	0.11
240	0	15.17	20.12	0	35.30	0.12
300	0	15.10	19.70	0	34.81	0.12
420	0	14.79	19.69	0	34.48	0.11
540	0	14.77	19.59	0	34.36	0.11
750	0	14.79	19.60	0	34.39	0.11
930.	0	0	19.59	0	19.59	0.06
1170	0	14.84	19.62	0	34.46	0.11
1440	0.47	15.57	20.32	0	35.89	0.12
2160	70.21	26.96	19.77	0	116.95	0.40
2880	127.8	0	19.66	0	147.48	0.51

As shown in Figure 5.13, the reference tap water has total THM concentration as 288.57µg/L but after continuous filtration for 2880 minutes, its total level reduced by 50%.

As Figure 5.14 demonstrates, the plot shows that the adsorbent is very effective and it took 2880 minutes to reach 50% level.

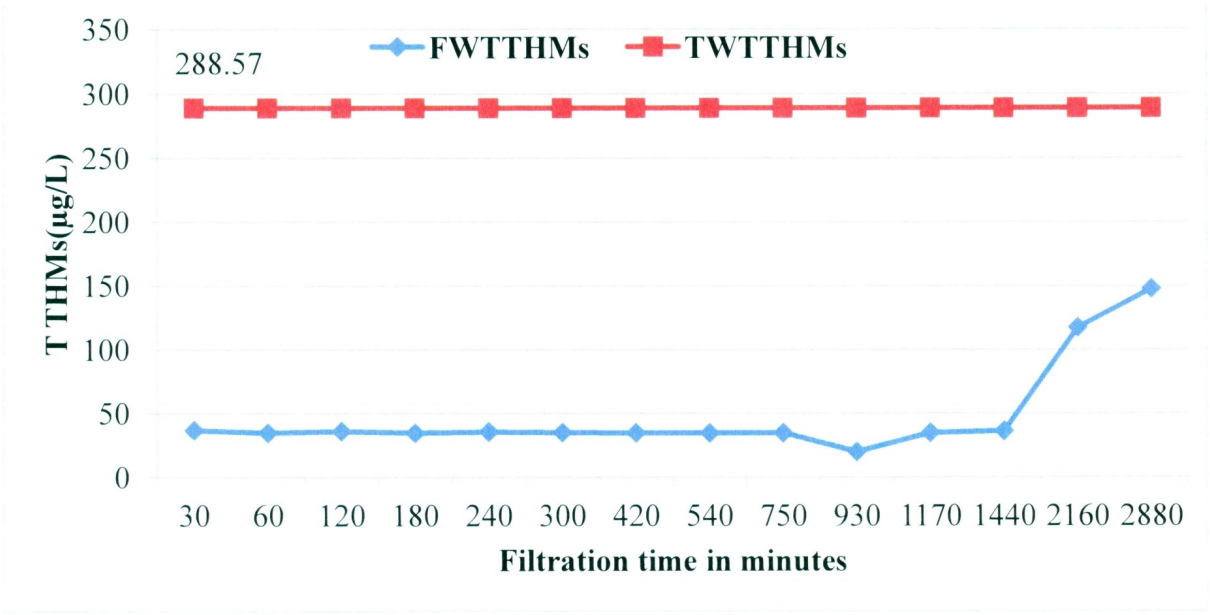

Figure 5-13 TTHMs concentration in filtered water with time of filtration

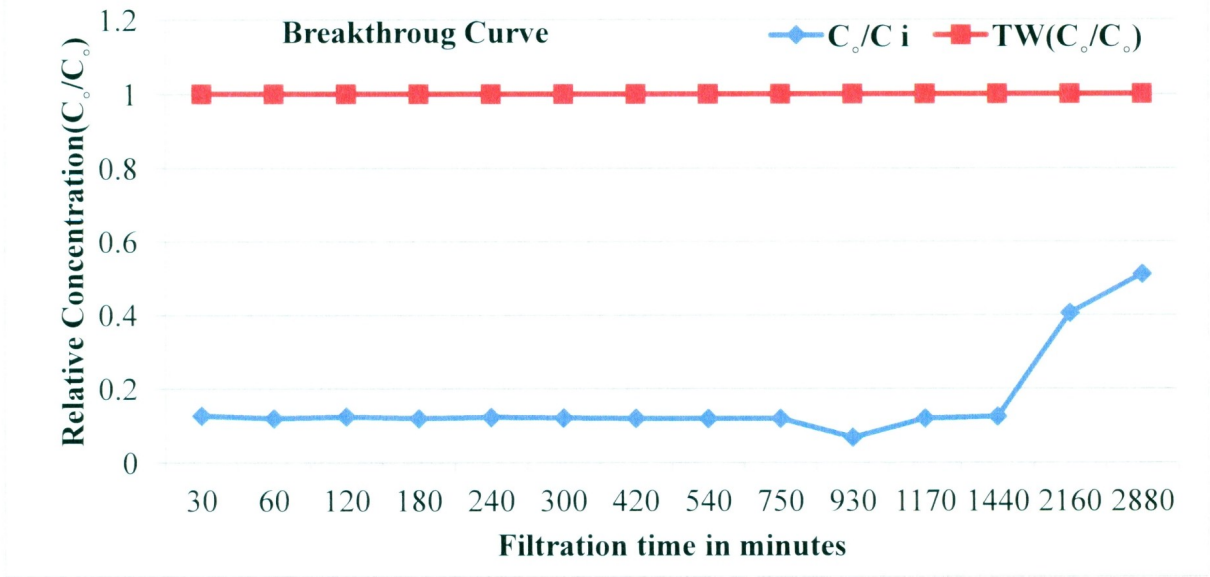

Figure 5-14 Relative concentration (C_o/C_i) of THMs with time of filtration

5.5.2 THM removal from tap water in Torbay

The filtration media is very effective in removing chloroform and BDCM from THM group. As shown in Table 5.13, chloroform level which was 79.25µg/L in tap water it was reduced to 52.80 µg after 3060 minutes of filtration. BDCM which was 29.77µg/L was reduced to 26.72 µg/L.

Table 5.13 THM compounds in tap water before and after filtration in Torbay community (µg/L)

Time(minute)	Chloroform	BDCM	DBCM	Bromoform	TTHMs	C_e/C_i
Tap water before filtration	79.25	29.77	21.37	22.60	153.014	1
Filtered water(30)	0	14.70	19.75	22.48	56.95	0.37
60	0	14.71	19.69	22.13	56.54	0.36
120	0	14.78	19.67	22.36	56.81	0.37
180	0	14.78	19.64	22.07222	56.50	0.36
240	0	14.77	19.62	22.06	56.46	0.36
300	0	15.41	20.33	28.77	64.52	0.42
420	0	15.27	19.61	22.03	56.92	0.37
540	0	15.80	19.63	22.52	57.96	0.37
660	0	14.84	19.60	22.05	56.51	0.36
940	27.79	0	19.73	22.02	69.56	0.45
1020	32.40	0	19.67	22.02	74.09	0.48
1200	0	0	19.60	22.32	41.93	0.27
1380	30.42	16.510	19.61	22.02	88.57	0.57
1620	0	19.99	19.61	0	39.61	0.25
2340	16.26	15.77	19.86	0	51.89	0.33
3060	52.80	26.72	19.89	22.18	121.61	0.79

In Figure 5.15, reference tap water has a total THM concentration as 153.35µg/L before filtration, but after filtration, the total THM concentration reduced considerably. As Figure 5.16 shows the adsorption efficiency by the filtrations media is above 60%.

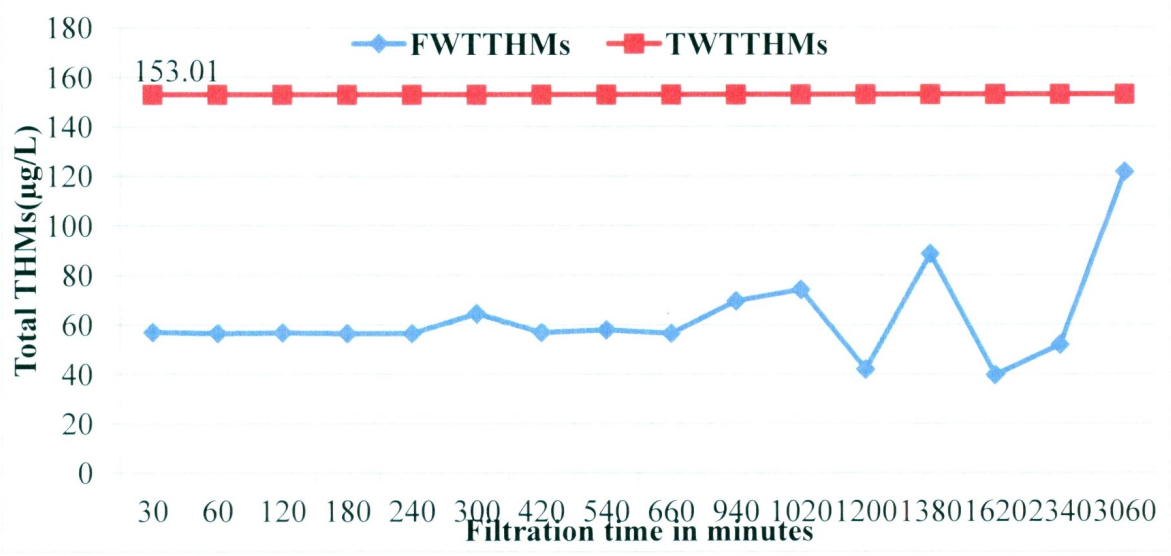

Figure 5-15 Graph between Time and TTHM concentration

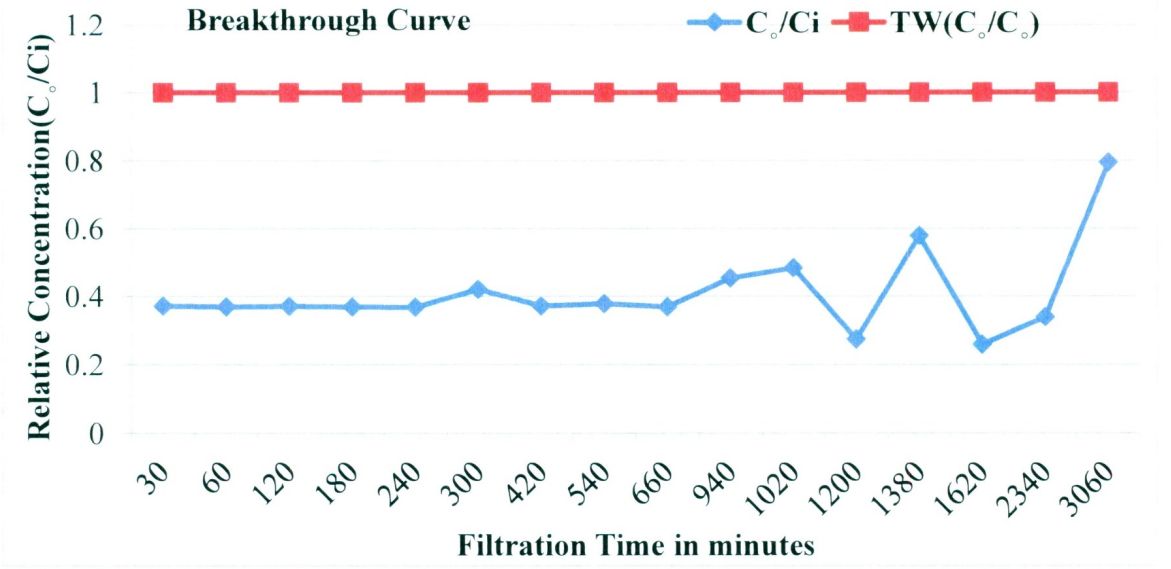

Figure 5-16 Relative concentration (C_0/C_i) trend with time of filtrat

5.6 HAA removal through using clean carbon

5.6.1 HAA removal from tap water in Pouch Cove

The clean carbon was found very effective in the removal of HAA compounds especially DCAA, TCAA, BCAA, DBAA and DBCAA. Table 5.14 shows the concentration of these compounds as 163 μg/L, 7.14 μg/L, 233.85μg/L, 25.31μg/L, and 20.47μg/L in the reference tap water respectively. After filtration for up to 480 minutes, these compounds were completely removed. Beyond 480 minutes of filtration, the concentration of these compounds started to increase gradually. TBAA was completely removed in the filtered water supply system.

Table 5.14 HAA compounds in tap water and filtered water in Pouch Cove community ((µg/L)

Time(minute)	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA	C_o/C_i
Tap water before filtration	0	0	163.69	7.14	233.85	0	25.31	0	20.47	450.48	1
Filtered water(30)	0	0	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0	0	0
180	0	0	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0	0	0
300	0	0	0	0	0	0	0	0	0	0	0
420	0	0	0	0	0	0	0	0	0	0	0
540	0	0	105.05	0	0	0	0	0	0	105.05	0.23
750	0	0	209.45	7.20	0	0	0	0	0	216.66	0.48
930	0	0	141.46	10.28	58.20	0	0	0	0	225.60	0.50
1170	0	0	204.31	9.72	55.46	0	0	0	0	343.49	0.76
1440	0	0	168.60	8.82	51.12	0	21.48	0	0	299.22	0.66
2160	0	0	29.99	4.88	31.92	0	22.65	0	0	109.61	0.24
2880	0	0	150.56	6.57	40.17	0	23.8	0	0	210.49	0.46

In Figure 5.17, reference tap water had total HAAs as 450.5µg/L, but after filtration, the concentration reduced considerably. As shown in Figure 5.18, the curve shows that after 2880 minutes of filtration the concentration was very low in the filtered water. This means that the adsorption efficiency of clean carbon was very high compared to activated carbon.

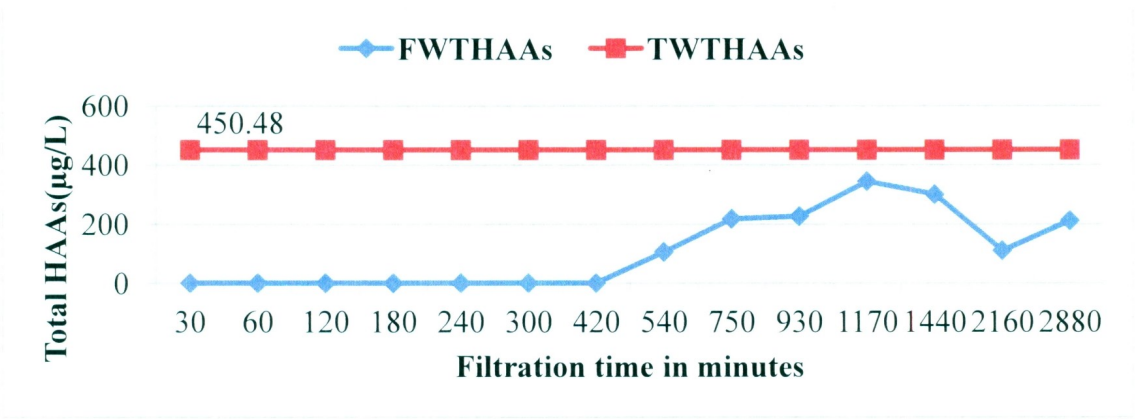

Figure 5-17 Graph between Time and THAAs concentration

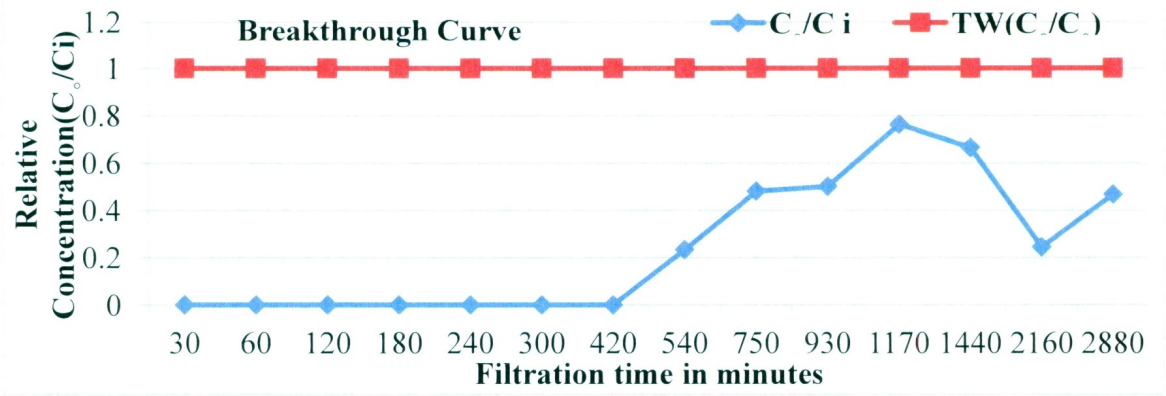

Figure 5-18 Relative concentration (C/C i) with filtration time

5.6.2 HAAs removal from tap water in Torbay

The adsorbent was found very effective on the removal of DCAA, TCAA, BCAA, and DBCAA. The pattern observed in Torbay is almost the same as in the Pouch Cove tap water using filtration by clean carbon. As demonstrated in Table 5.15, in the first 300 minutes, all nine compounds were removed by the carbon. After 420 minutes of filtration, the efficiency gradually decreased and the concentration of HAAs compounds gradually increased.

Table 5.15 HAA compounds in tap water and filtered water in Torbay community (µg/L)

Time(minute)	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA	C_o/C_i
Tap water before filtration	0	0	26.60	4.483	48.91	0	22.51	0	0	102.50	1
Filtered water(30)	0	0	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0	0	0
180	0	0	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0	0	0
300	0	0	0	0	0	0	0	0	0	0	0
420	0	0	58.48	2.83	0	0	0	0	0	61.31	0.59
540	0	0	37.57	7.69	0	0	0	0	0	45.26	0.44
660	0	0	59.49	10.32	0	0	0	0	0	69.82	0.68
940	0	0	77.80	7.54	39.42	0	0	0	0	124.76	1.21
1020	0	0	50.86	8.00	41.80	0	0	0	0	100.66	0.98
1200	0	0	41.11	6.38	48.89	0	0	0	0	96.39	0.94
1380	0	0	0	6.64	69.82	0	0	0	0	76.46	0.74
1620	0	0	0	6.13	64.44	0	24.42	0	0	95.00	0.92
2340	0	0	0	6.39	54.91	0	26.00	0	0	87.31	0.85
3060	0	0	29.65	4.64	53.09	0	22.69	0	0	80.43	0.78

In Figure 5.19, the total HAAs concentration is 102.5µg/L before filtration. After filtration, the total HAAs concentration only reached to 80.52µg/L.Figure 5.20 in the breakthrough curve shows that even after 3060 minutes of filtration, it did not reach to the reference level.

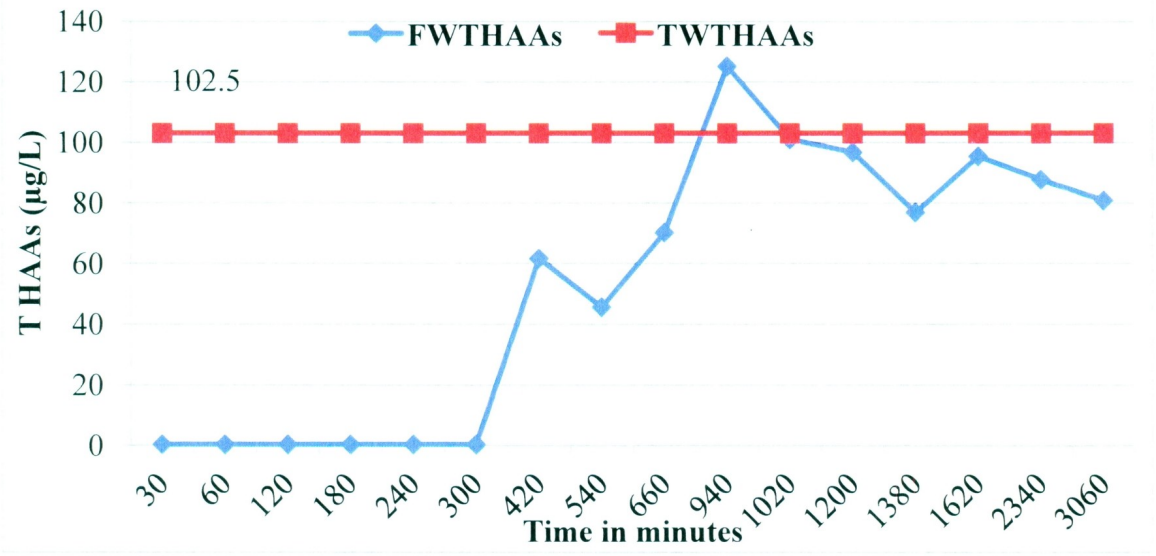

Figure 5-19 Graph between Time and THAAs concentration

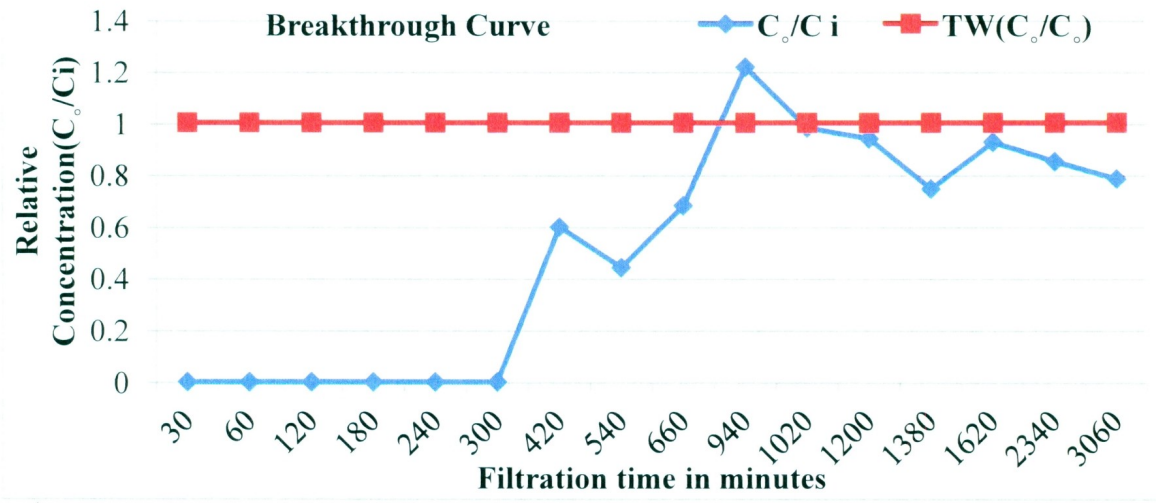

Figure 5-20 Breakthrough Curve between relative concentration(C₀/C i) and Time

In order to assess water quality after filtration, samples were analysed using ICP-MS and the results are listed in Table 5.16. As shown in the table, most of the parameters were non-detectable and were below the levels specified by the US EPA and the Canadian guidelines.

Table 5.16 Maximum Limit of heavy metals in the drinking water and comparison with Canadian and EPA guide line standards

Metal (mg/L)	U.S EPA guide line May 2009(mg/L)	Health Canada guide line August 2012(mg/L)	After Filtration with Clean Carbon(mg/L)	After filtration with activated carbon	Raw water(mg/L)
Arsenic(As)	.01	.01	ND	ND	ND
Cadmium(Cd)	.005	.005	ND	ND	ND
Chromium(Cr)	.1	.05	ND	.001	ND
Copper(Cu)	1.3	<1	.092	.0076	.047
Mercury(Hg)	.003	.001	ND	ND	ND
Lead (Pb)	< .015	.01	.002	.004	.002
Selenium (Se)	.05	ND	ND	ND	ND
Vanadium(V)	5251.471	221.321	ND	ND	ND
Zinc(Zn)	5.0	< 5	.937	.464	.001

5.7 Pouch Cove raw water quality

After filtration of tap water with the clean carbon, the results were very encouraging in the removal of THMs but with marginal gain on HAAs removal. There

are two ways to reduce the formation of DBPs: first, by the application of a filtration media on tap water and second method is by reduction of the organic precursors from the raw water. The first application and the results are discussed above while the second option to reduce precursors, mainly total organic carbon (TOC) from the source water is discussed below.

The raw water samples used in this study were collected from the North Three Island Pond, which is the distribution source for Pouch Cove community. The parameters such as TOC, pH, UV254, turbidity, and color of the water were measured and the results are tabulated in Table 5.17. The results show high level of TOC in the intake water and turbidity above 1 NTU.

The column test was conducted to study the trend of TOC removal by adsorbent. For this column test experiment was set up by using pyrex glass column with the dimension of 30 cm in length and 40mm in internal diameter, and 64g of clean carbon was added. The experiment setup details are shown in Figure 5.4. In order to prevent the leaching of the fine particles into the filtered water, glass wool and 1μm filter at the outlet of the column were used. The test was conducted using the raw water. A flow rate of 3.5 ml/min was maintained through the column, and for this a peristaltic pump was used. The filtered water was collected at different time intervals. The advantage of using a peristaltic pump in this experiment was that there was no cross contamination since water flowing through the column did not touch any mechanical part of the pump and water passed through the internal tubing system. The filtered samples were analysed for the

TOC concentration, pH, Turbidity and UV_{254}. The raw water passes through the column and is filtered through clean carbon. The TOC of raw and filtered water were analysed to determine the removal efficiency of TOC, as tabulated in Table 5.17. The adsorbent was found very effective in the removal of TOC from the Pouch Cove community raw water

Table 5.17 Intake water quality and reduction in TOC in Pouch Cove community before and after filtration

Time(minute)	PH	Uv254(cm)	Turbidity(NTU)	TOC(mg/L)	% TOC Reduction	C_o/C_i
Raw water before filtration	6.61	0.13	1.45	13.64	0	1
After filteration240	6.14	0.007	0.35	1.16	92	0.08
540	6.7	0.01	0.34	1.04	93	0.076
960	6.63	0.03	0.34	2.10	85	0.15
1620	6.43	0.01	0.36	5.7	58	0.41
2940	6.4	0.005	0.4	6.73	53	0.49
3720	6.51	0.01	0.38	4.90	64	0.35
4020	6.71	0.05	0.34	5.49	60	0.40
4440	6.72	0.005	0.33	5.64	50	0.41
5100	6.65	0.001	0.36	5.45	52	0.40
6000	6.72	0.001	0.35	6.84	39	0.50
7500	6.74	0.001	0.37	5.56	50	0.40

As shown in Figure 5.21, the parameter such as TOC, UV254 and turbidity were high in the raw water and the pH value was within the range of 6.5 and 8.5. Figure 5.22 shows percentage reduction in the TOC with the time of filtration. Initial TOC reduction was 92% for 240 minutes of filtration but after this, the TOC removal efficiency started decreasing and after 7500 minutes of filtration, TOC concentration removal reached 50%.

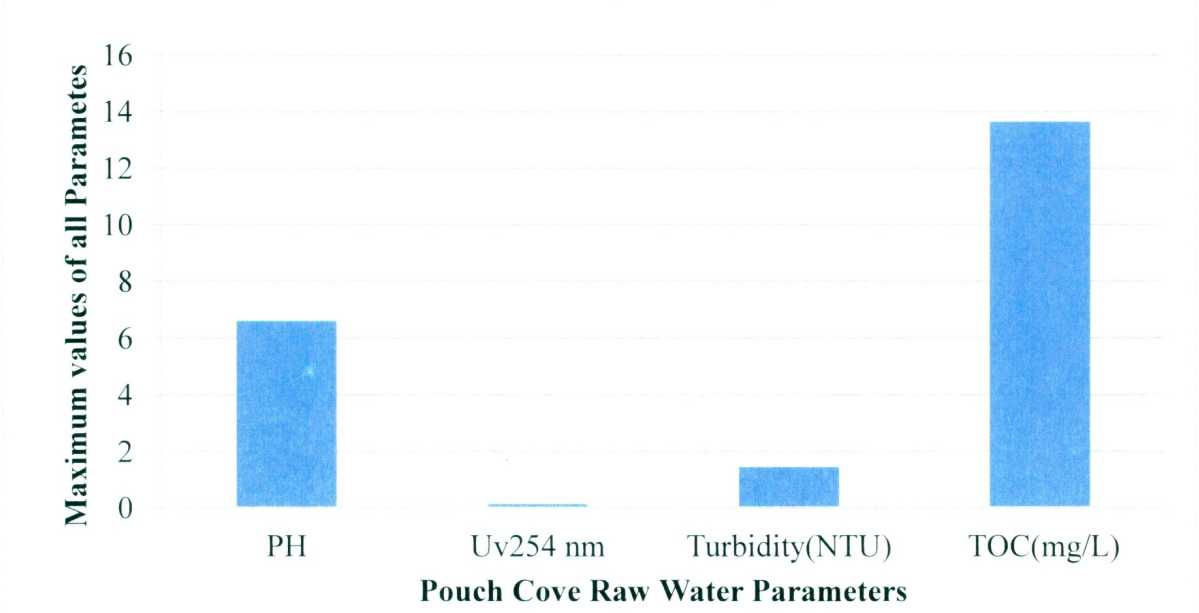

Figure 5-21 Pouch Cove raw water characterization

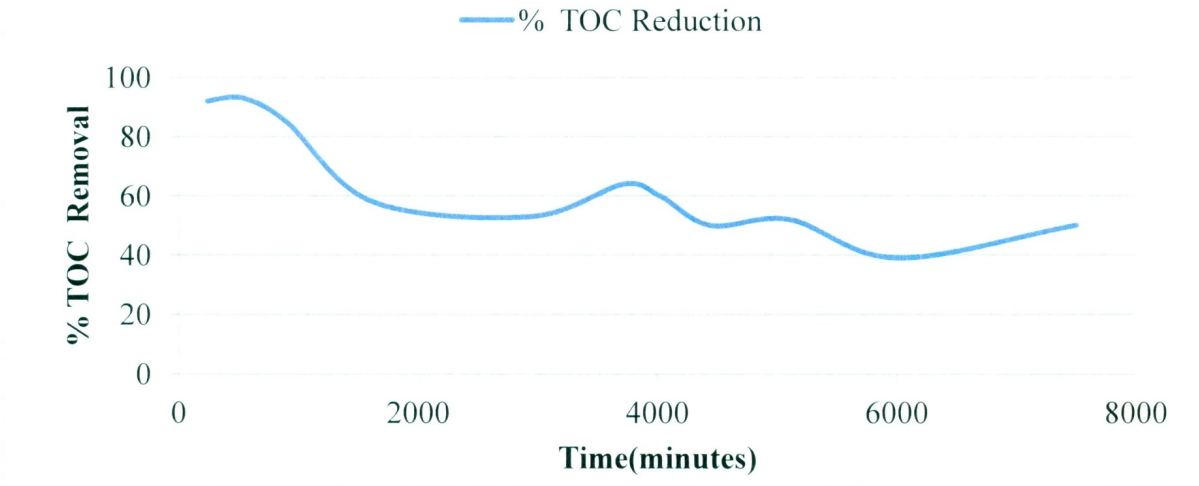

Figure 5-22 TOC % reductions for different timing of filtration– Pouch Cove intake water

As shown in Figure 5.23, the initial concentration of TOC in the raw water was 13.64 mg/L, but after 7500 minutes filtration it reached up to 5.56 mg/L. It means that the adsorbent which is clean carbon is very effective in TOC removal from the Pouch Cove raw water.

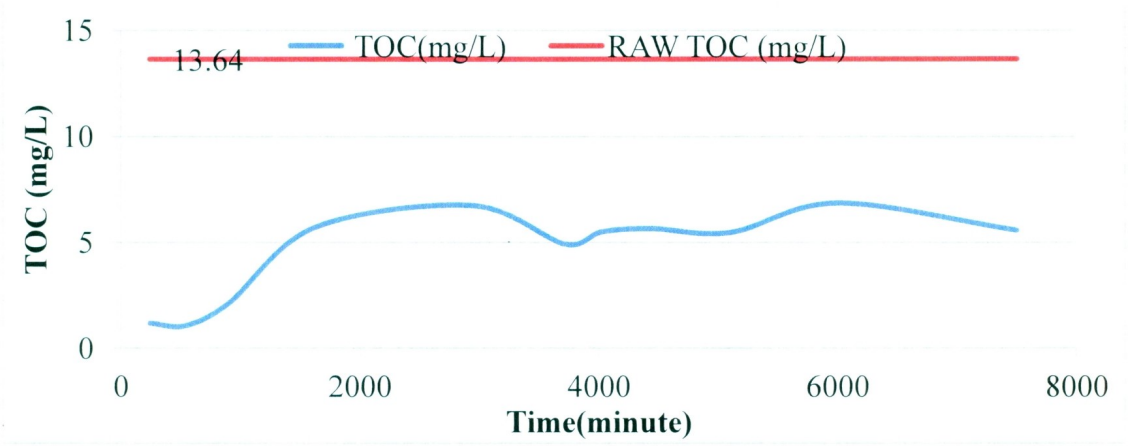

Figure 5-23 Changes in TOC with filtration – Pouch Cove intake water

As shown in Figure 5.24 to 5.27, the UV254, pH ,and turbidity concentration were within the range according to the Canadian drinking water guide line. The pH rang is 6.5 to 8.5 and Turbidity range .5 NTU. UV254 range is not available.

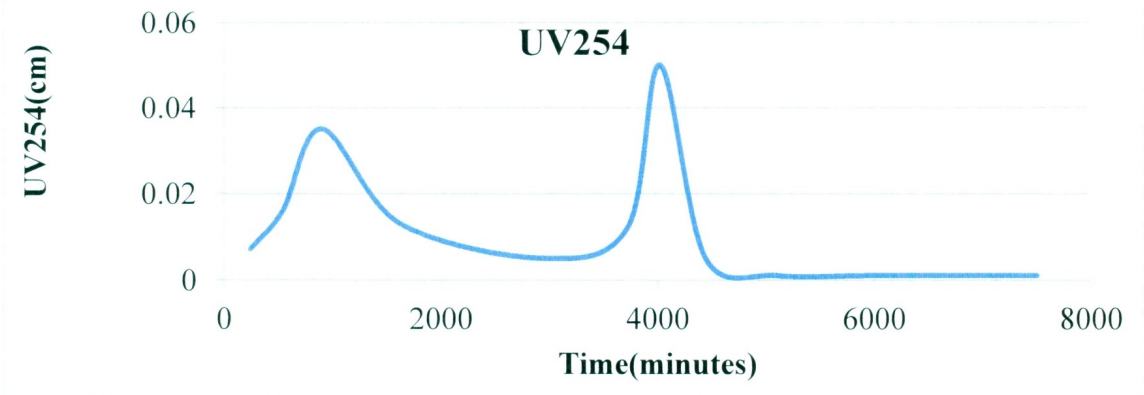

Figure 5-24 Changes in UV254 with filtration– Pouch Cove intake water

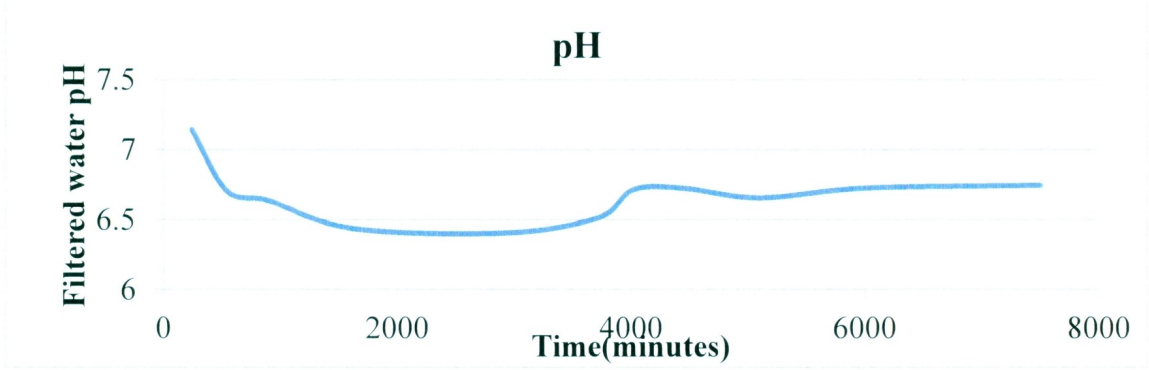

Figure 5-25 Changes in pH with filtration– Pouch Cove intake water

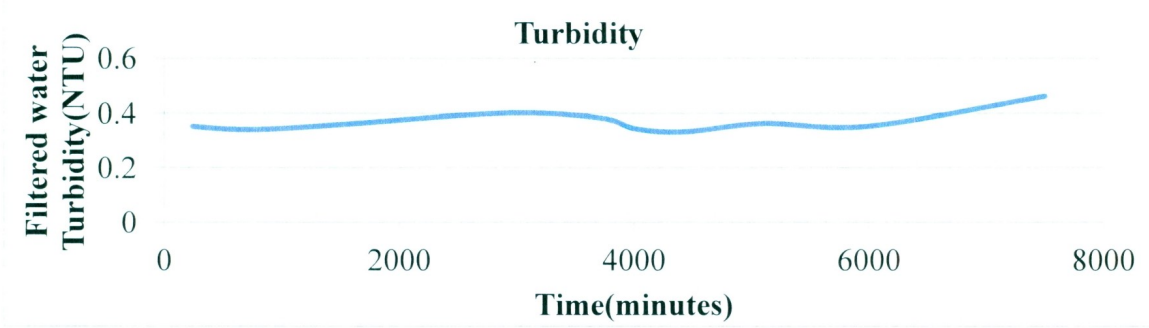

Figure 5-26 Changes in turbidity with filtration – Pouch Cove intake water

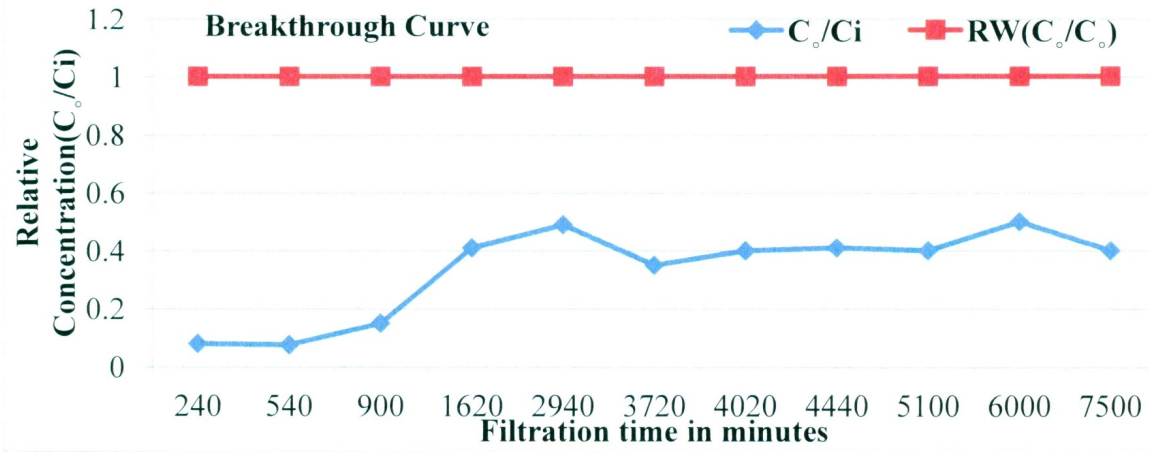

Figure 5-27 Relative concentration of TOC in filtered water

5.7.1 Torbay source water quality

The raw water samples were collected from the North Pond, which is the distribution source for the Torbay community and measured values of the parameters such as TOC (mg/L), pH, UV254, turbidity are listed in Table 5.18. The TOC of raw water was 5.41 mg/L while turbidity was lower than the raw water from Pouch Cove intake source.

Table 5.18 Intake water quality and reduction in TOC in Torbay community before and after filtration

Time(minutes)	pH	UV254(cm)	turbidity (NTU)	TOC(mg/L)	% Reduction	C_0/C_i
Raw water before filtration	6.23	0.02	0.59	5.41	0	1
After filtration240	5.64	0.04	0.31	1.31	76	0.24
540	5.79	0.002	0.35	1.86	66	0.34
960	5.8	0.003	0.42	1.70	69	0.31
1560	5.76	0.04	0.43	1.83	66	0.18
2880	5.99	0.06	0.39	3.37	38	0.62
3600	6.01	0.042	0.33	2.37	56	0.43
3960	6.43	0.02	0.42	2.08	40	0.38
4200	6.51	0.009	0.35	2.57	55	0.47
4740	6.75	0.007	0.36	2.74	52	0.50
5700	6.74	0.13	0.37	2.87	49	0.53
7200	6.82	0.003	0.34	3.31	41	0.61

As shown in Figure 5.28 the raw water parameter including TOC, UV254, and turbidity values were normal and within the range. Figure 5.29 shows initial TOC reduction was 76% after 240 minutes of filtration but after 7500 minutes filtration, TOC concentration removal reached at 41 %.

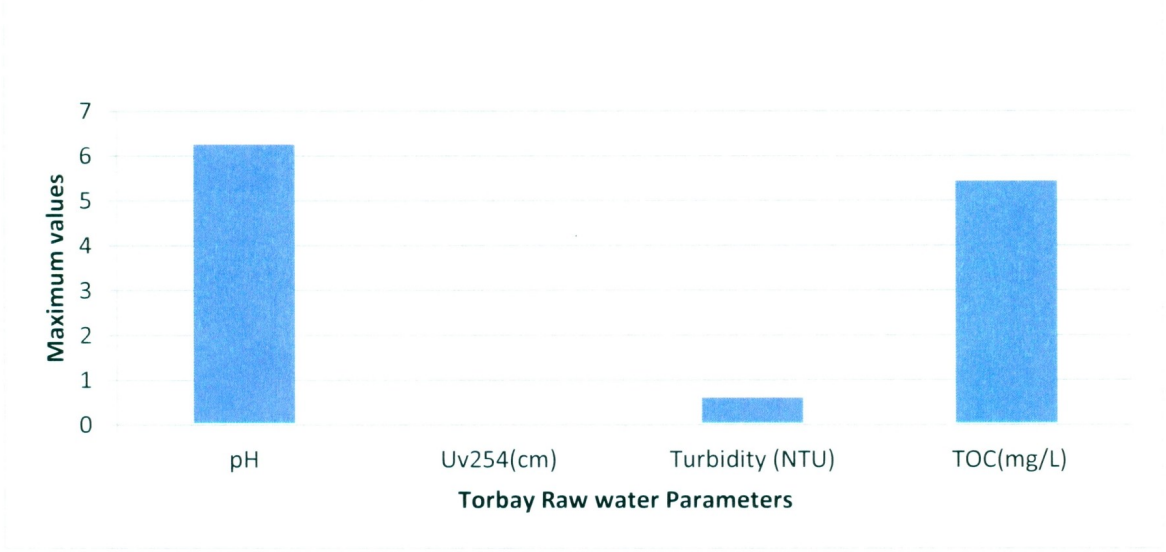

Figure 5-28 Torbay Raw water quality

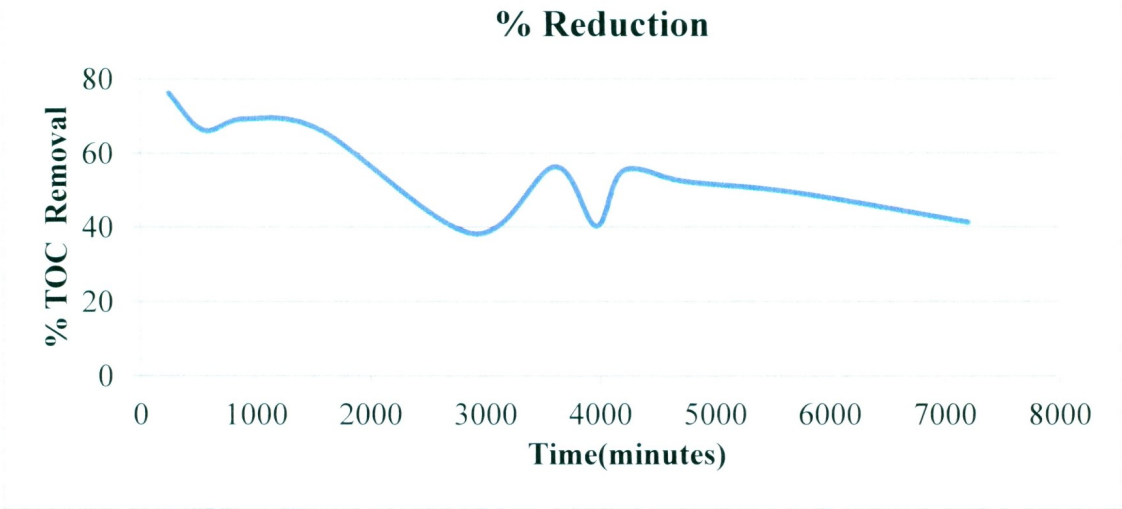

Figure 5-29 Percent reduction in TOC with filtration – Torbay intake water

Figure 5.30 shows variation in TOC concentration with respect to time. Figures 5.31 to Figure 5.34 show the UV254, pH ,and turbidity concentration within the range specified by the Canadian drinking water guidelines.

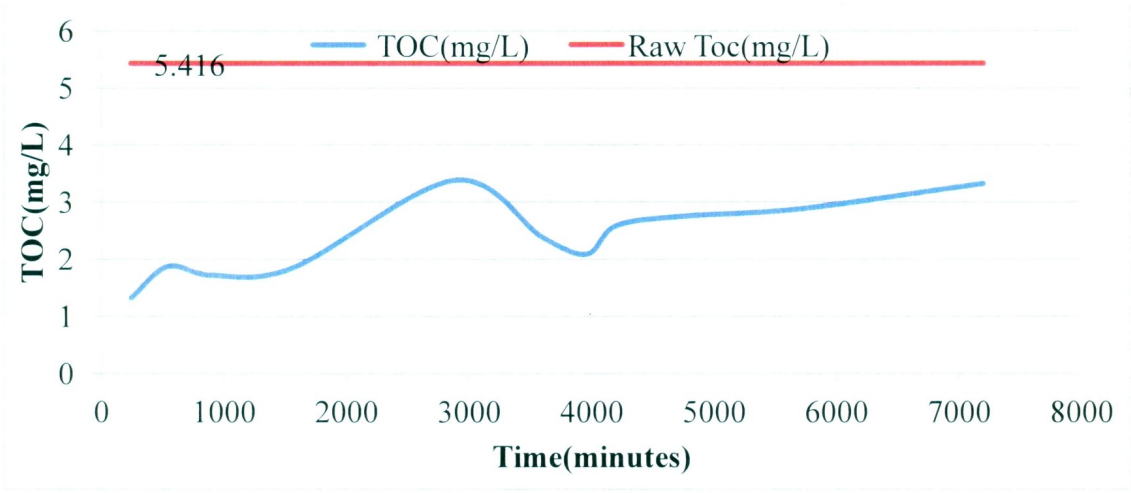

Figure 5-30 Changes in TOC with filtration– Torbay intake water

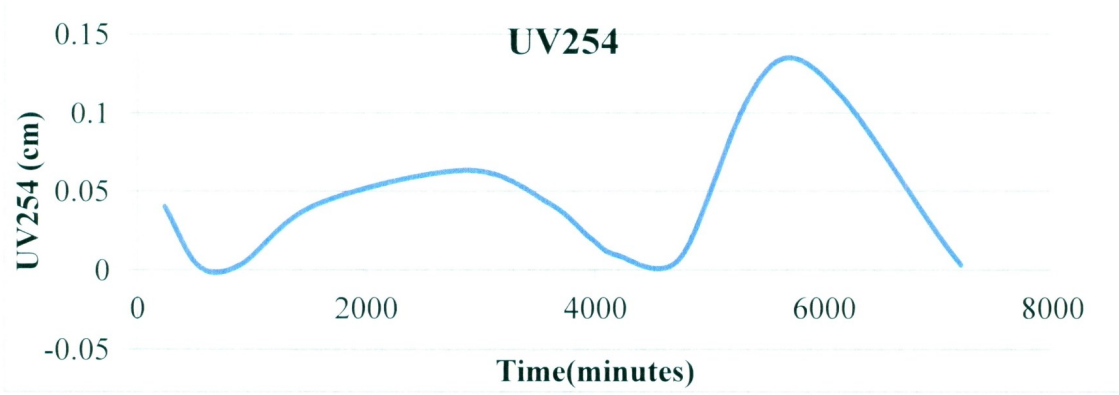

Figure 5-31 Changes in UV 254 with filtration – Torbay intake water

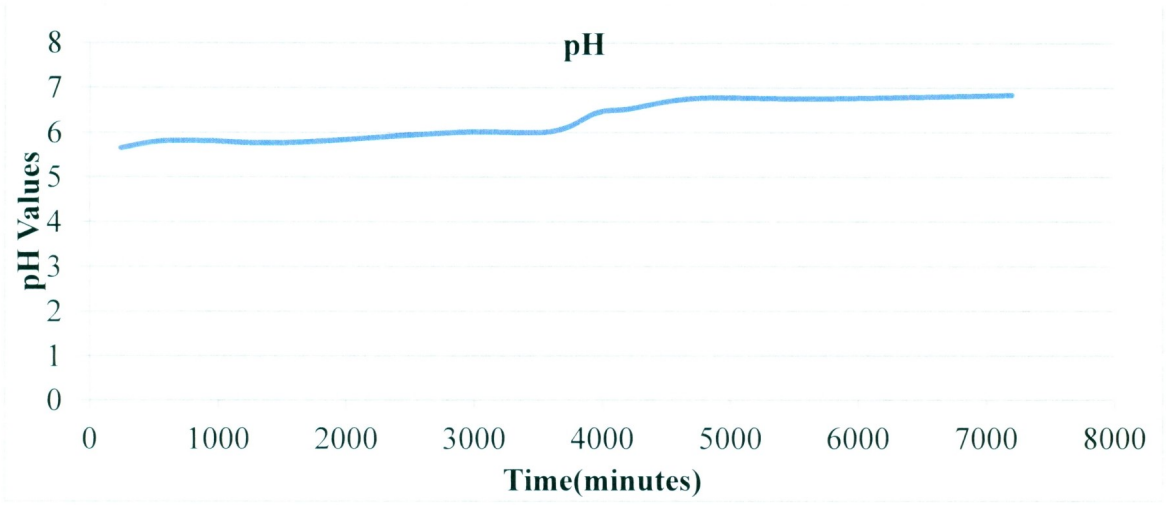

Figure 5-32 Changes in pH with filtration – Torbay intake water

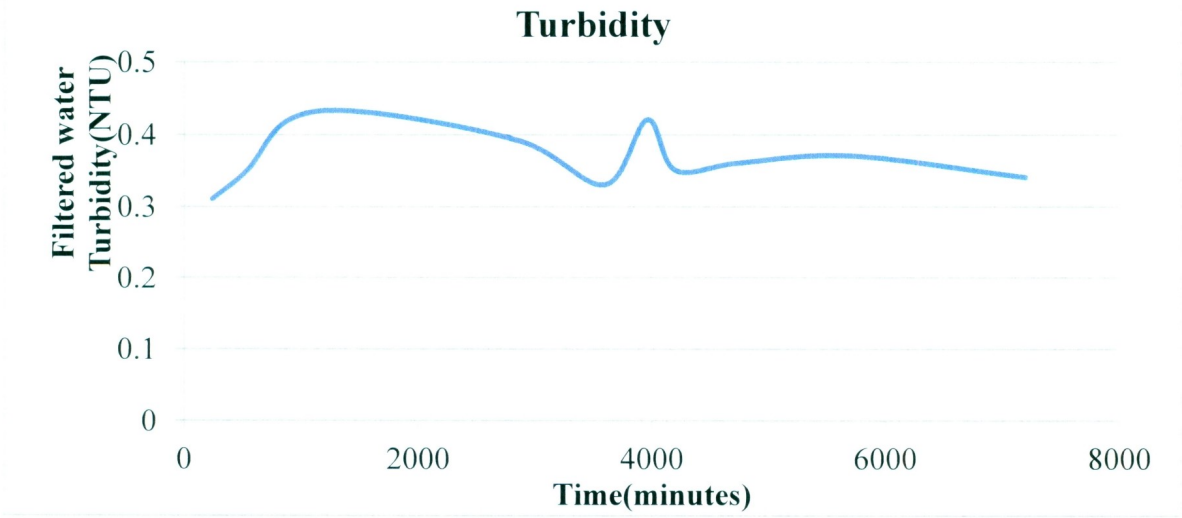

Figure 5-33 Changes in turbidity with filtration – Torbay intake water

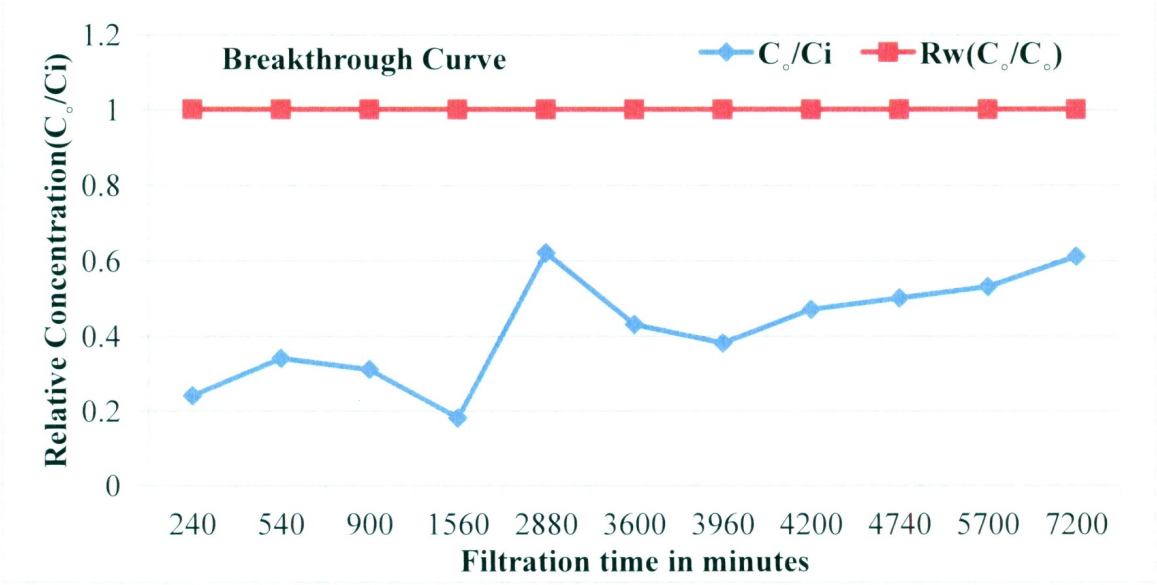

Figure 5-34 Relative TOC level in filtered water – Torbay intake water

Chapter 6 Formation Potential of THMs and HAAs in Intake Water

6.1 Formation Potential of THMs in Intake Water

6.1.1 Formation Potential of THMs – Pouch Cove Intake Water

The mechanism of formation of DBPs in the water depends on the NOM and their concentration in water before adding disinfectant as well as the retention time in the water supply system. Once disinfectants are added in the water, some by-products or DBPs are formed in the presence of natural organic matters (NOM) in the water supply system.

In this study, the samples collected after 4, 16, 74 and 125 hrs of filtration with TOC concentrations 1.16, 2.1, 5.64 and 5.56 mg/L respectively were chlorinated to study DBPs formation potential in the filtered water. Similarly the raw water with TOC concentration 13.64 mg/L was also chlorinated. An attempt was made to maintain same residual chlorine level in both filtered and raw water samples. For chlorination, aqueous Sodium Hypochlorite was used. The THMs formation in both filtered and raw water was studied with the contact time of 4, 12, 18 and 24 hrs. After that water samples were analysed for THMs as shown in the Table 6.1.

As shown in the table, the levels of chloroform, and BDCM were significantly low in the filtered water compared to the raw water for the same contact time. The other two compounds such as DBCM and bromoform have no significant changes.

Table 6.1 Pouch Cove THMs Filtered and Raw water Data

Pouch Cove Raw Water	Dose mg/l	Contact time(hrs)	Filtration time(hrs)	Chloroform	DCBM	DBCM	Bromoform	RTTHMs	FTTHMs	EPA TTHMs	Canadian TTHMs
	8	4	0	144.38	55.30	36.10222	22.18	257.97		80	100
	8	12	0	155.60.	55.85	36.48	22.25	270.20		80	100
	8	18	0	179.39	60.089	36.28	22.17.	297.94		80	100
	8	24	0	165.22	57.083	36.09	22.16	280.57		80	100
Pouch Cove Filtered water	8	4	4	28.44	29.07	35.12	22.25		114.90	80	100
	8	12	16	27.91	28.78	34.95	22.23		113.88	80	100
	8	18	74	44.47	42.44	39.61	22.13		148.6677	80	100
	8	24	125	52.88	43.61	39.32	22.23		158.06	80	100

As shown in Figure 6.1 the individual concentration of THMs compounds such as chloroform, BDCM, DBCM and bromoform were very high and gradually decreased in raw water with different contact times.

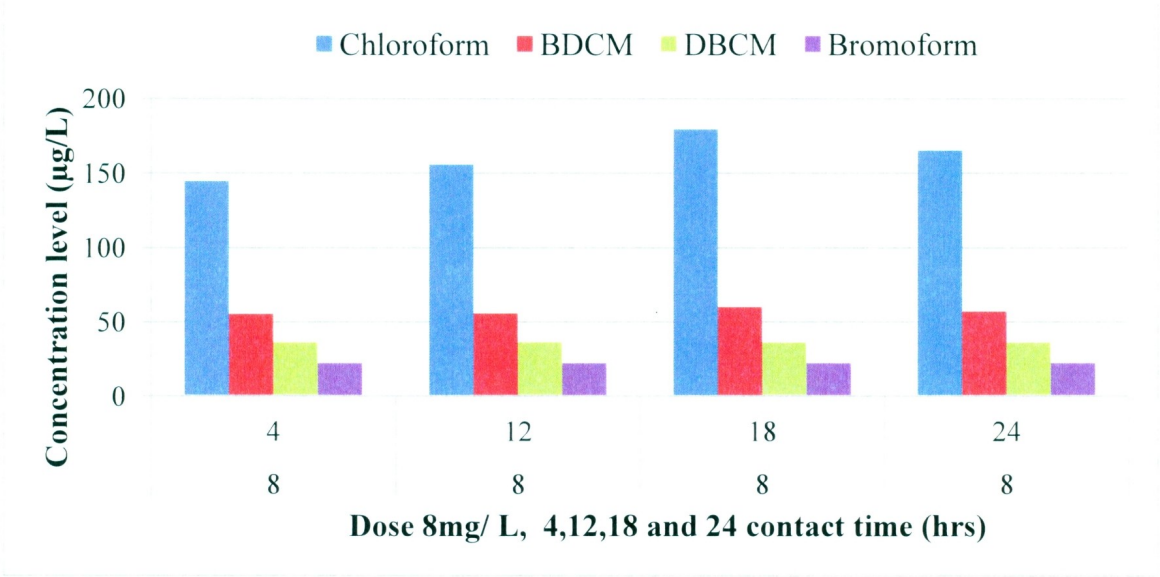

Figure 6-1 Individual THM compounds in raw and filtered water for different contact times

As shown in the Figure 6.2, filtered water with a 1.16, 2.10, 5.64 and 5.56 mg/L TOC level, have significantly lower THMs compounds than in the raw water.

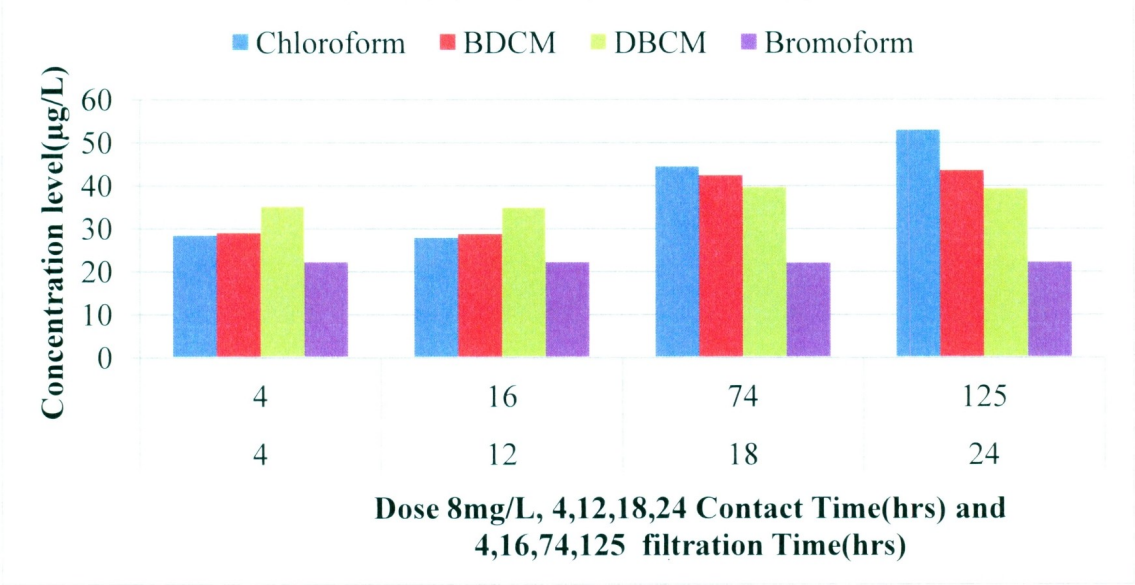

Figure 6-2 Individual THM in raw and filtered water for different contact time

As shown in the Table 6.2 and Figure 6.3, the total concentration of raw water THM concentration was very high as compared to the treated water.

Table 6.2 Total THM in raw and filtered water

Pouch Cove raw water TTHMs µg/L		Pouch Cove Filtered water TTHMs µg/L			
Contact Time(hrs)	RPTTHMs	FPTTHMs	Filtration time	EPA TTHMs	Canadian TTHMs
4	257.978	114.90	4	80	100
12	270.2026	113.88	16	80	100
18	297.9412	148.66	74	80	100
24	280.577	158.06	125	80	100

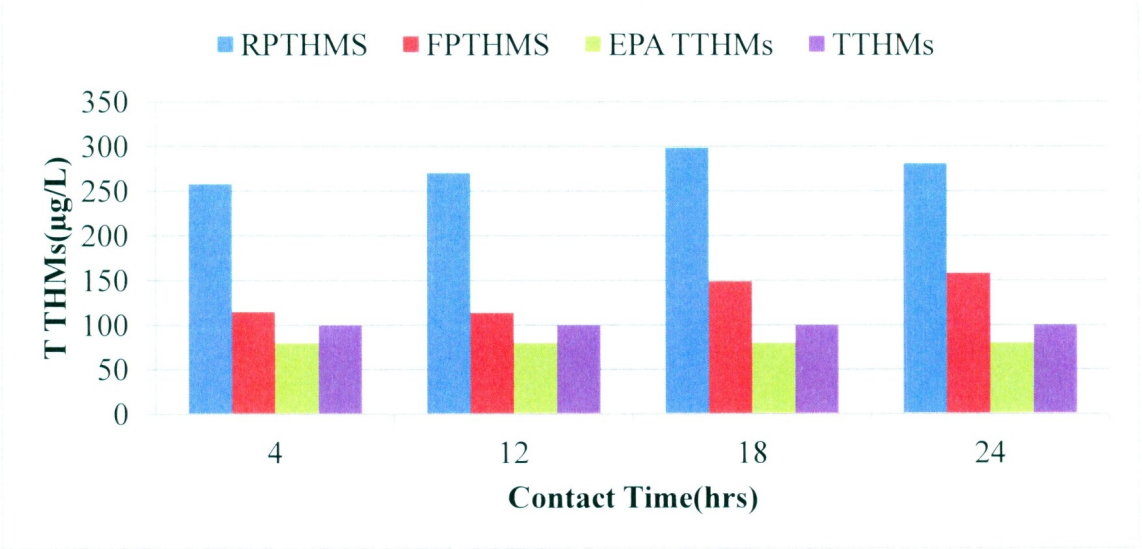

Figure 6-3 Total THM in raw and filtered water and comparison with guidelines

6.1.2 HAAs after chlorination of Pouch Cove Raw and Filtered Water with different Contact Times

After analysing the sample for HAAs as shown in Table 6.3, the concentration of all nine HAAs except BCAA were very low in the filtered water, compared to the concentration in the raw water.

Table 6.3 Individual HAAs in raw and filtered water – Pouch Cove intake source

	Dose mg/L	Contact time(hrs)	Filtration Time (hrs)	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	PRTHAA	PFTHAA
Pouch Cove raw water	8	4	0	0	0	14.27.	13.87	140.12	0	23.79	0	0	192.0683	0
	8	12	0	0	0	15.81	11.5	176.15	0	22.34	0	0	225.8292	0
	8	24	0	0	0	8.61	10.86	189.94	0	22.36	0	0	231.7967	0
Pouch Cove Filtered water	8	4	4	0	0	0	0	11.33	0	0	0	0	0	11.33
	8	12	16	0	0	0.75	0	13.78	0	19.77	0	0	0	34.31
	8	24	154	0	0	1.38	12.36	17.04	0	21.09	0	0	0	39.52

As shown in Figure 6.4, only DCAA, TCAA, BCAA and DBAA compounds show high levels in the raw water after chlorination and the concentration of these compounds increased gradually with increase in contact time after chlorination.

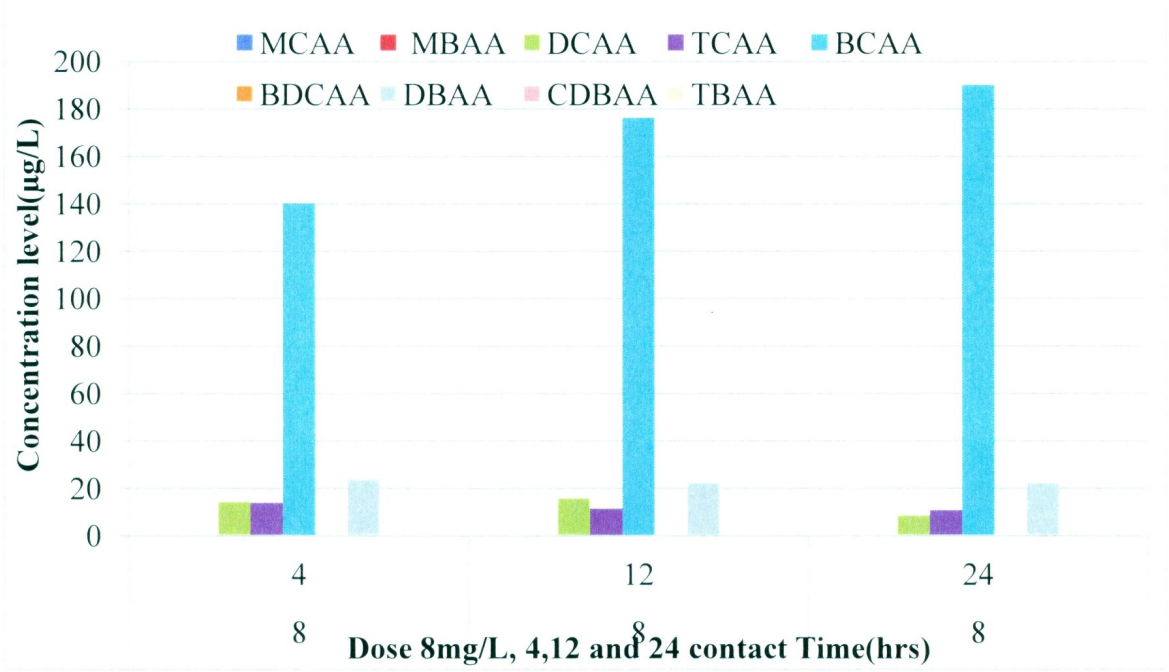

Figure 6-4 Individual HAAs in raw and filtered water with different contact time

Figure 6.5 shows treated water with different level of TOC concentration. In the first 4 hours contact time, only one compound BCAA became visible. After 12 hours DCAA, TCAA, BCAA and after 24 hours contact time, DCAA, TCAA, BCAA and DBAA appeared and their concentration gradually increased.

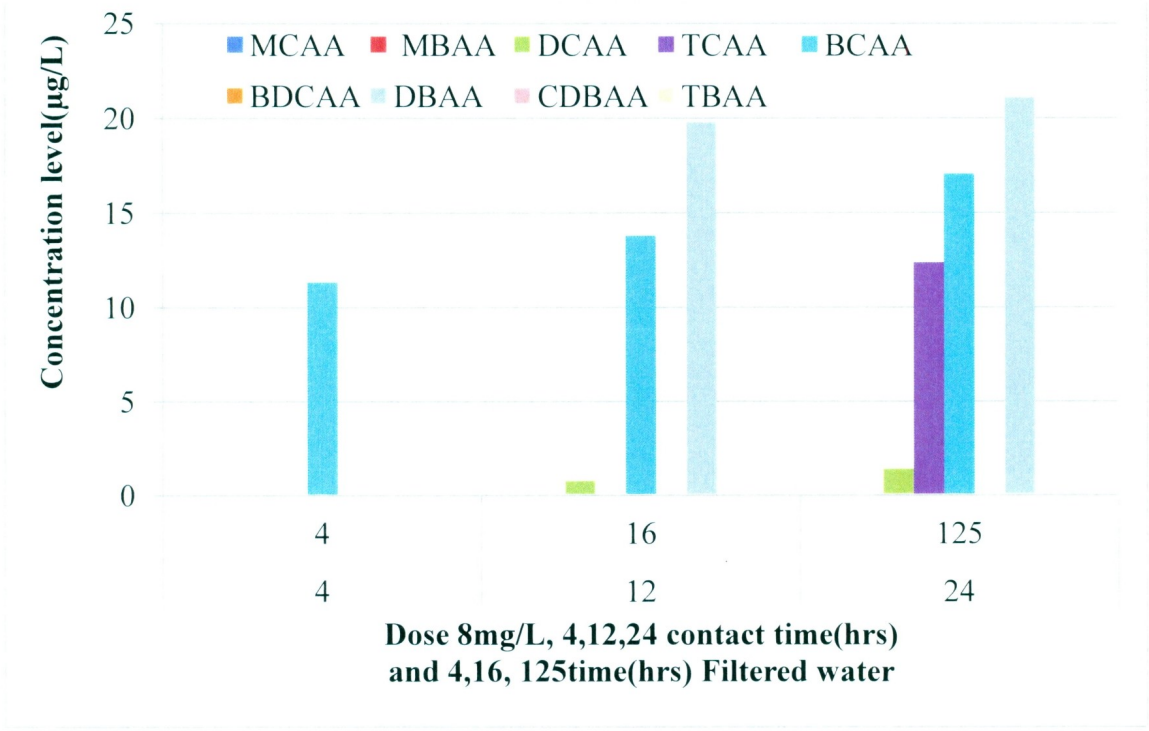

Figure 6-5 Individual HAA compounds in raw and filtered water

As shown in the Table 6.4 and Figure 6.6, the total HAAs concentration in raw water with high TOC is higher than in the treated water with low TOC values.

Table 6.4 Total HAAs in raw and filtered water in Pouch Cove intake source

Pouch Cove raw water		Pouch Cove Filtered water			
Contact Time(hrs)	RTHAAs	FTHAAs	Filtration time(hrs)	EPA THAAs	Canadian THAAs
4	192.06	11.33	4	60	80
12	225.82	34.31	16	60	80
24	231.79	39.52	125	60	80

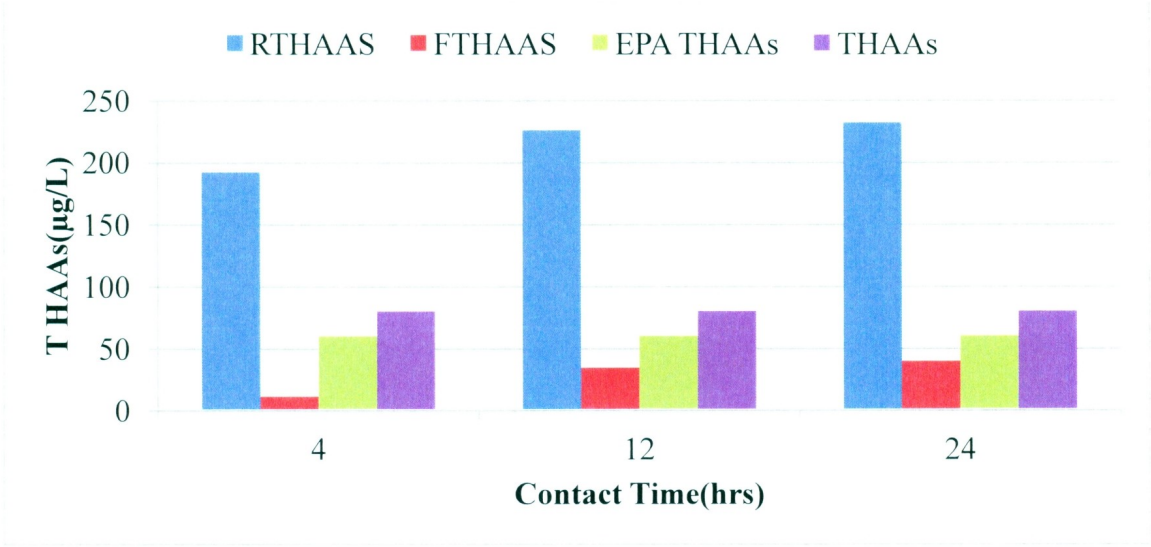

Figure 6-6 Total HAAs in raw and filtered water in Pouch Cove intake source

6.2 Formation Potential of THMs in Torbay Intake Water

6.2.1 THMs analysis after chlorination of Torbay Intake and Filtered water with different Contact Times

As shown in the Table 6.5, in the chlorinated raw water all four compounds of THMs were much higher than in the treated water with low TOC value. This pattern is almost the same in Pouch Cove community water system. The chloroform and BDCM concentration significantly decreased in the treated water. The other two compounds in THM group such as DBCM and bromoform do not have any significant changes in both treated and raw water.

Table 6.5 Individual THM compounds in raw and filtered water in Torbay intake source

Raw Water Torbay	DOSE(mg/L)		Filtered water Timing(hrs)	Chloroform	BDCM	DBCM	Bromoform	RTTHMs	FTTHMS	EPA TTHMs	TTHMs
	8	4	0	56.97.	72.95	35.31	22.91	188.15	0	80	100
	8	12	0	625.50	67.008	34.73	22.54	749.79	0	80	100
	8	18	0	468.05	76.73	34.97	22.26	602.03	0	80	100
	8	24	0	624.56	62.78	34.43	22.21	743.99	0	80	100
Filtered water Torbay	8	4	4	27.02	27.60	36.08	22.18		112.90	80	100
	8	12	16	34.65	34.26	36.80	22.12		127.84	80	100
	8	18	74	257.93	67.84	35.52	22.05		383.37	80	100
	8	24	120	304.14	72.79	35.45	22.08		434.48	80	100

As shown in the Figure 6.7, the Chloroform concentration is more dominating as compared to other three compounds of THMs.

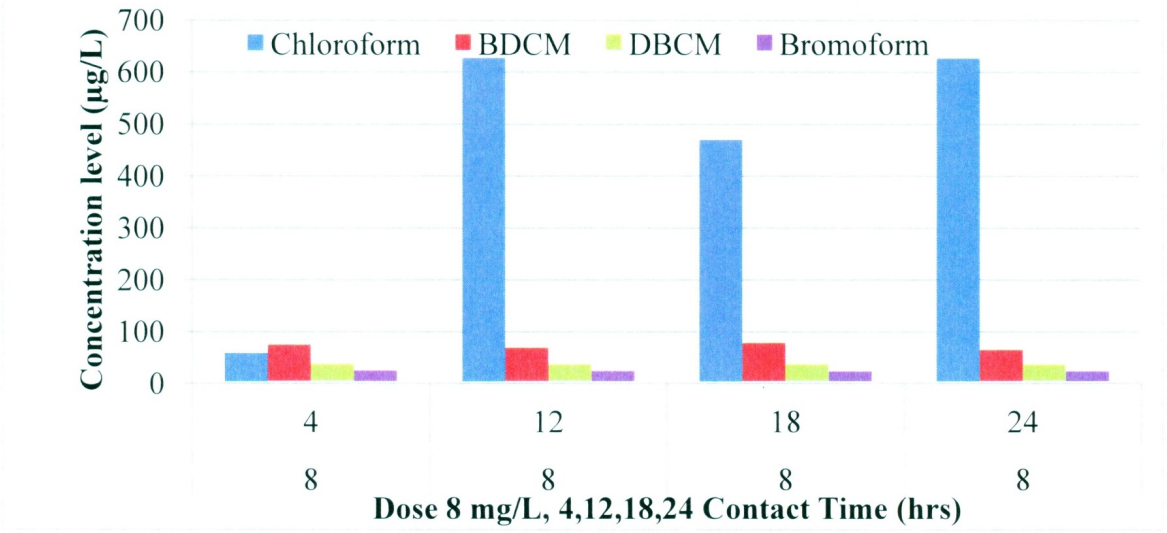

Figure 6-7 Individual THM in raw and filtered water with different contact times

As shown in the Figure 6.8 the individual compounds of THMs in the treated water gradually increased with respect to time and its TOC values increased in raw water level.

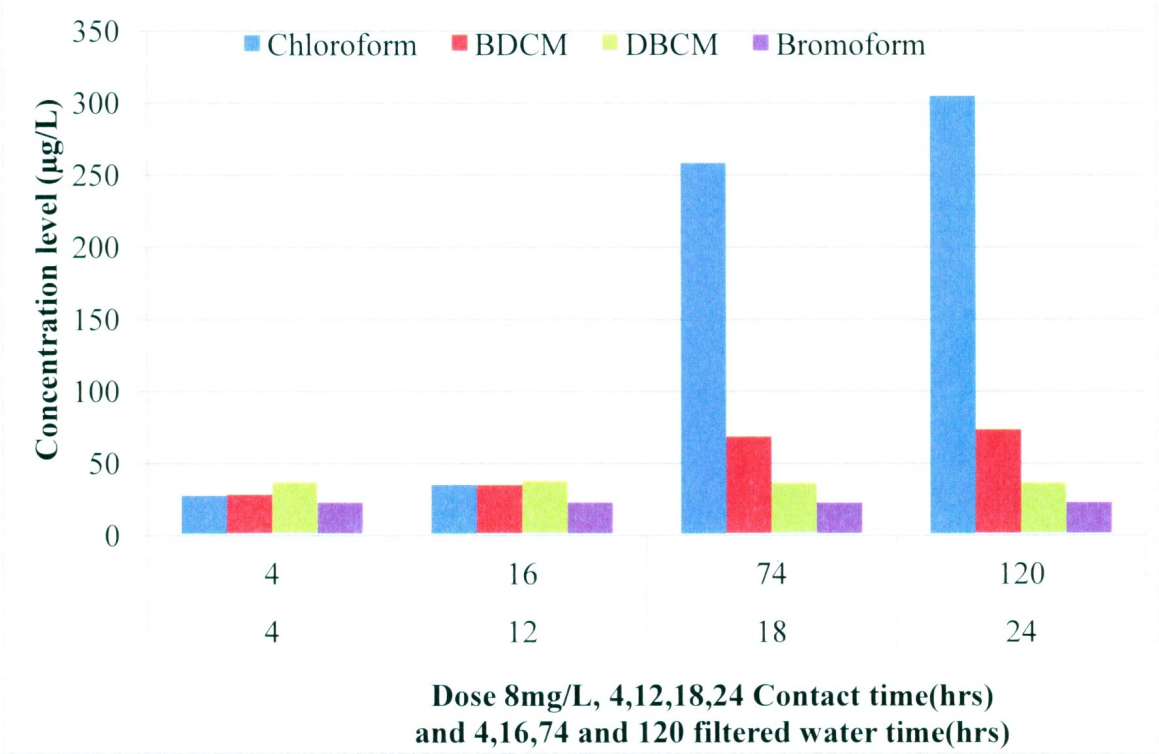

Figure 6-8 Individual THM compounds in raw and filtered water with different contact times

The samples collected after 4, 16, 74 and 120 hrs of filtration with 1.31, 1.7, 2.57 and 3.31 mg/L respectively were chlorinated to study DBP formation potential in the filtered water. Similarly the raw water with TOC concentration 5.56 mg/L. As shown in Table 6.6 and Figure 6.9 due to difference in concentrations of TOC in the raw water and the filtered water, total concentration of THMs is higher in the raw water than in the filtered water.

Table 6.6 Total THM potential in raw and filtered water

Torbay raw water		Torbay Filtered water			
Contact Time(hrs)	RTTHMs	FTTHMs	Filtration time	EPA TTHMs	Canadian TTHMs
4	188.15	112.90	4	80	100
12	749.79	127.84	16	80	100
18	602.03	383.37	74	80	100
24	743.99	434.48	120	80	100

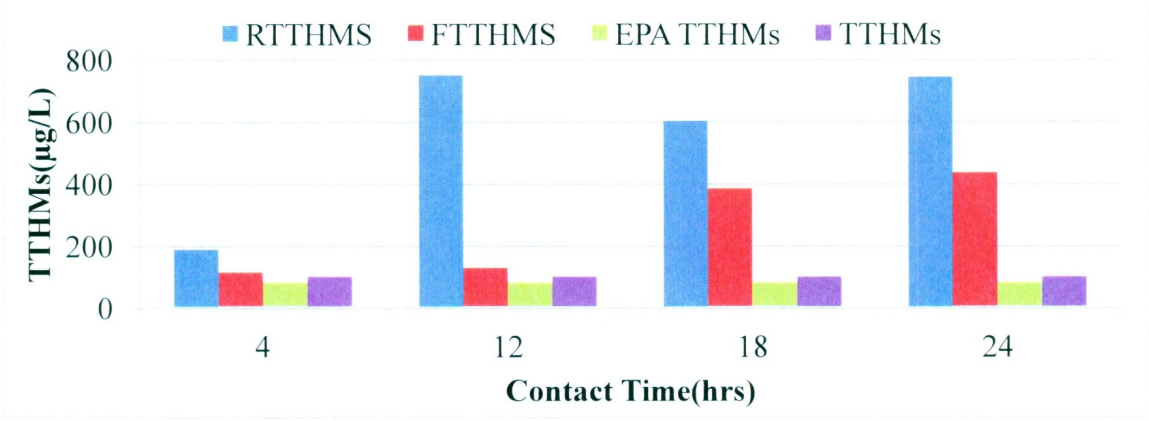

Figure 6-9 THM potential in raw and filtered water with different contact times

6.2.2 HAAs after Chlorination in Torbay raw and Filtered Water with different Contact Times

As shown in Table 6.7 and Figure 6.10 we found concentration of DCAA, TCAA, BCAA and DBAA to be very high in the raw water.

Table 6.7 Individual HAAs in raw and filtered water – Torbay intake water system

	Dose mg/L	Contact Time (hrs)	Filtered water (hrs)	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	TRHAA	TFHAAs
Raw water Torbay	8	4	0	0	0	7.08	13.58	82.08	0	24.73	0	0	127.47	0
	8	24	0	0	0	5.81	12.61	65.98	0	22.40	0	0	106.81	0
Filtered water Torbay	8	4	4	0	0	0	0	11.56	0	0	0	0	0	11.56
	8	24	120	0	0	16.21	17.46	83.05	0	23.46	0	0	0	140.20

Figure 6.10 shows that, for raw water and in Figure 6.11 for filtered water, high level of BCAA were found but other compounds in the filtered water were very low. A similar trend was observed in Torbay water as in the Pouch Cove community water.

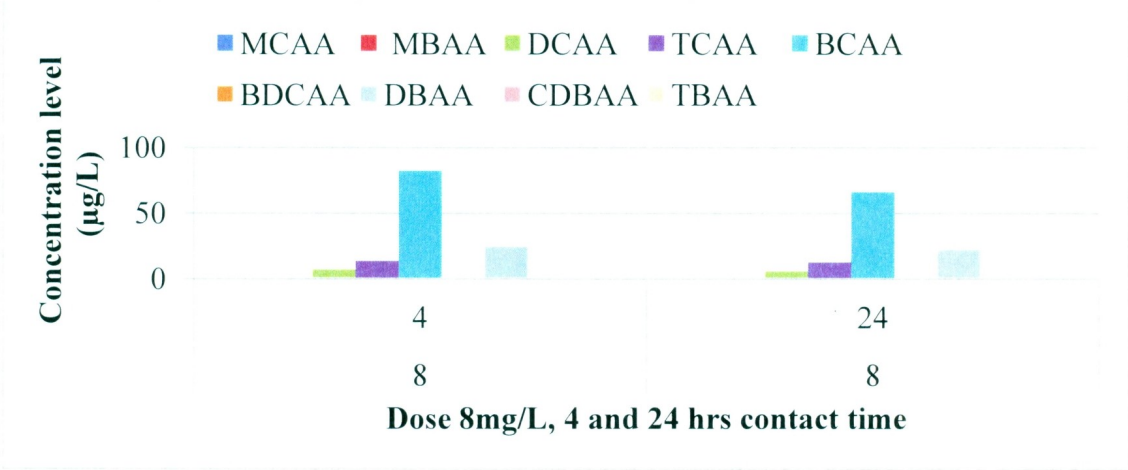

Figure 6-10 Raw water HAAs individual compounds concentration with same dose and different contact time (hrs)

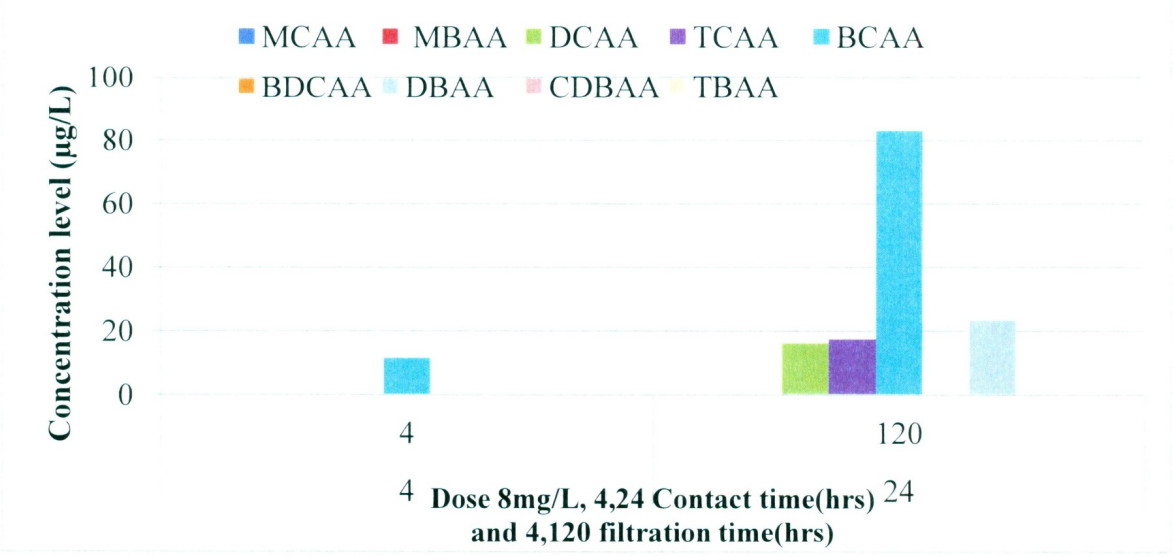

Figure 6-11 Individual HAAs concentration in filtered water with same dose and different filtration and contact time(hrs)

As shown in the Table 6.8 and Figure 6.12, the total concentration of HAAs in raw water is much higher than of treated water.

Table 6.8 Formation potential of HAAs in raw and filtered water with different contact times

Torbay raw water		Torbay Filtered water		
Contact Time(hrs)	RTHAAs	FTHAAs	EPA THAAs	Canadian THAAs
4	127.47	11.56	60	80
24	106.81	140.20	60	80

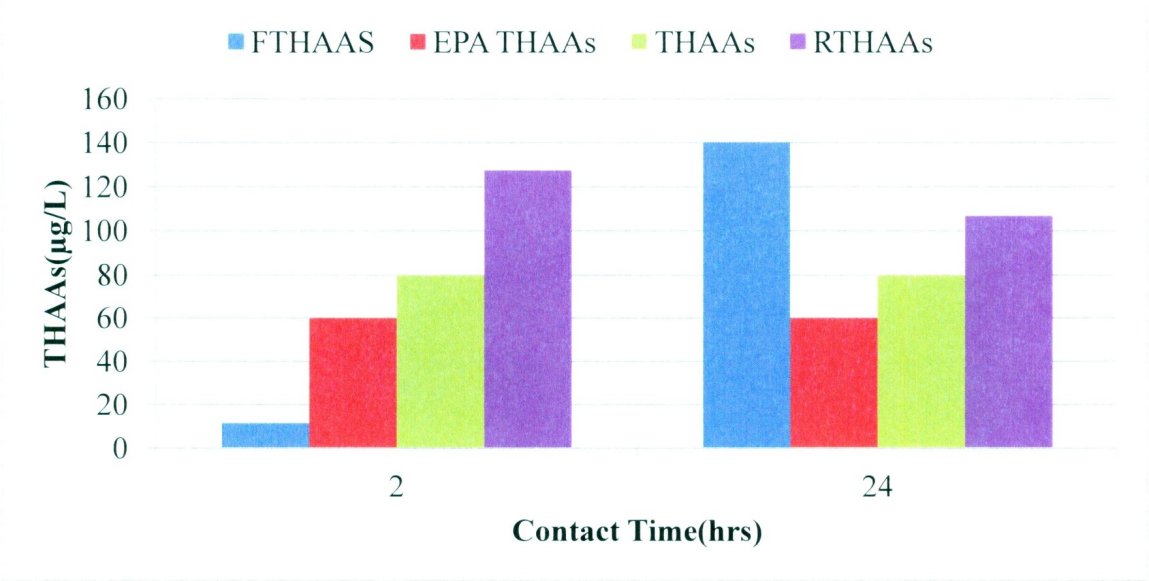

Figure 6-12 Formation potential of HAAs in raw and filtered water with different contact time

Chapter 7 Conclusions

Although there are different types of treatment methods such as membrane filtration, coagulation, reverse osmosis and other adsorption processes available to reduce THMs and HAAs in the drinking water systems but most of these methods require trained personnel to operate and maintain the system and requires high capital investment. Due to lack of skilled personnel to operate and maintain water systems and also high capital cost, it is not feasible to install such systems in small communities. The main objective of this study was to identify a cost effective adsorbent to remove DBPs and their precursors. The adsorbent developed from ash residues can be easily used at very low incremental cost. In this research, the extracted adsorbent was tested with a series of experiments using raw and treated water from the Pouch Cove and Torbay communities near St. John's. The results showed a significant removal of DBPs and their precursors. This study also shows that the developed product, clean carbon, can be used as an effective and inexpensive filtration media for the removal of THMs and HAAs in the water supply system. This adsorbent also has a great potential in providing safe drinking water to the rural communities.

The following main conclusions are drawn from this study.

1. The batch test results of the Pouch Cove tap water showed significant reduction of chloroform, BDCM, and DBCM, with on overall reduction by 95% of THMs while BDCAA and TBAA in the HAAs group were reduced but with a total reduction of 35% only. The performance of activated carbon is assessed using column test on tap water from Torbay and Pouch Cove water supply systems and found very

effective in the removal of chloroform. After 15 hours of filtration, chloroform concentration was reduced by 75%. There was also a significant reduction in the BDCM but the concentrations of DBCM and bromoform were unchanged. The chloroform levels in the Torbay Community water were 259 µg/L which reduced to 56µg/L (75% reduction) after a continuous filtration for 15 hours. Similarly the BDCM levels reduced from 38µg/L to 5µg/L (more than 85% reduction).The reduction in the DBCM and bromoform levels was approximately 50%. For Pouch Cove, activated carbon was effective in the removal of chloroform while for the Torbay community it was effective in the removal of all compounds within the THM group.

2. The column test was performed with clean carbon for the community of Pouch Cove and Torbay tap water. For Pouch Cove tap water, more than 50% of THMs were removed with a continuous run for 48 hours while the removal efficiency was less than 50% for Torbay water. The extracted clean carbon removed more than 95% of HAAs from the Pouch Cove tap water for a continuous filtration for seven hours. A similar trend was observed in the Torbay tap water. The clean carbon adsorbent was also used to assess its performance for TOC removal. TOC is considered as a precursor of DBPs in the intake sources of communities of Pouch Cove and Torbay. The TOC concentration in Pouch Cove raw water was 13.64 mg/L. After 15 hours of filtration it was reduced to 2.1 mg/L so the reduction was more than 85% and 150 hours of filtration, TOC was reduced to 5.56 mg/L.

3. The TOC in the Torbay raw water was 5.41mg/L. After 120 hours of filtration, TOC was reduced to 3.3 mg/L with 41% reduction. There was also considerable reduction in turbidity and UV absorbance, which indicates an overall improvement in the quality of water in both communities.
4. To assess the formation THMs and HAAs in the raw water in the communities of Pouch Cove and Torbay with different levels of TOC values, the raw water and the filtered water were chlorinated with a fixed amount of chlorine dosage keeping the same contact times for both waters. The formation of the THMs of Pouch Cove showed that the chloroform and BDCM levels were 144.45 and 55.33µg/L respectively in the raw water for four hour contact time, while filtered water had only 28.44 and 29.07 µg/L chloroform and BDCM concentration, showing a significant decrease in the DBP formation in the treated water. A similar trend was observed in the Torbay intake water. HAA compounds such as DCAA, TCAA, BCAA and DBAA were 14.27, 13.87, 140.1, and 23.79µg/L respectively in the raw water at a four hour contact time. These compounds were completely eliminated in the filtered water

Chapter 8 Recommendations

Although the adsorbent used for this research has potential to remove DBPs from drinking water supply systems but the results reported in this work are based on limited data and require an in-depth investigation before its use as a filtration media. Some of the limitations are highlighted in this section with a summary for future research as follows.

1. Our analysis is based on very limited number of samples. In order to have a better understanding on the variation of THMs and HAAs in the tap water, more samples should be collected and analysed covering different seasons and times covering weekend and weekdays. Sample collection should also be done at different locations in the water distribution systems and records should be maintained on the type of pipe materials and size of pipes at the point of sampling.
2. The activated carbon used in this study was based on very preliminary work and limited samples. It is recommended to improve its adsorption capacity by micro-sieving of extracted carbon and using different physical and activation processes. Further research work on the preparation of activated carbon with chemical impregnation and homogenization is recommended.
3. **S**ince clean carbon is not very effective on the removal of HAAs, further research is needed to investigate its pre-treatment and activation process. Characterization should be done in this study.

4. The regeneration and backwashing of the adsorbent was not conducted in this study. It would be useful to develop feasibility of regeneration of adsorbent.
5. Since TOC values were performed only in summer months, more samples should be collected and analyzed covering temperature ranges in different seasons and hydrologic variations.
6. The residual chlorine in the tap water should be maintained to a level that it does not cause any microbial growth and at the same time, the levels should not be too high. In this research, a limited number of samples were chlorinated to study formation of THMs and HAAs potential with different contact time. It is suggested to conduct a detailed scientific investigation on the measurement of residual chlorine in the treated water with a better control on its level with different contact times up to 3 to 4 days.

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